Catalizadores basados en **materiales carbonosos** para procesos de **oxidación húmeda** con **peróxido de hidrógeno**

Tesis Doctoral, Madrid 2013
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Memoria
que para optar al grado de
Doctor con Mención Intermacional
presenta
Carmen María Domínguez Torre

Directores: Dr. José Antonio Casas de Pedro
Dra. Asunción Quintanilla Gómez

Madrid, 2013

D. José Antonio Casas de Pedro, Profesor Titular de Universidad y **Dña. Asunción Quintanilla Gómez**, Profesor Contratado Doctor, ambos profesores de la Sección Departamental de Ingeniería Química, perteneciente al Departamento de Química-Física Aplicada de la Universidad Autónoma de Madrid,

HACEN CONSTAR: que el presente trabajo, titulado: "Catalizadores basados en Materiales Carbonosos para Procesos de Oxidación Húmeda con Peróxido de Hidrógeno", presentado por Dña. Carmen María Domínguez Torre, ha sido realizado bajo su dirección, en los laboratorios de la Sección de Ingeniería Química, en la Universidad Autónoma de Madrid y que, a su juicio, reúne los requisitos de originalidad y rigor científico necesarios para ser presentado como Tesis Doctoral.

Y para que conste a efectos oportunos, firmamos el presente informe en Madrid, a 04 de diciembre de 2013.

José Antonio Casas de Pedro

Asunción Quintanilla Gómez

La realización del presente trabajo ha sido posible gracias al apoyo económico prestado a través de los proyectos CTQ2008-03988/PPQ, CTQ2010/14807, y S-2009-AMB-1588.

A mi familia y amigos

"Si buscas resultados distintos,
no hagas siempre lo mismo"

—Albert Einstein—

Índice

1

Estructura de la Tesis Doctoral

La presente Memoria de Tesis Doctoral consta de los apartados Introducción, Objetivos y Resultados y Discusión. A continuación se incluye un Resumen detallado del trabajo, en el que se recogen los aspectos más relevantes discutidos en los apartados anteriores. En último lugar, se presentan las Conclusiones finales de la presente investigación.

La Introducción de este trabajo tiene como objetivo contextualizar la problemática actual del agua y, en particular, la de las aguas residuales industriales, así como exponer las diferentes alternativas existentes para su tratamiento. Se da especial relevancia a los procesos de oxidación química, dentro de los cuales se encuentran los Procesos de Oxidación Avanzada (*Advanced Oxidation Processes, AOPs*), entre los que se ha puesto especial interés en los Procesos de Oxidación Húmeda Catalítica con Peróxido de hidrógeno (*Catalytic Wet Peroxide Oxidation, CWPO*), ya que es el proceso objeto de estudio de la presente Tesis Doctoral. Por este motivo, se han

analizado y discutido los resultados más relevantes obtenidos en las casi dos décadas de investigación en este campo. Esta minuciosa revisión bibliográfica pone de manifiesto los retos futuros que, una vez superados, permitirán la implantación industrial de esta tecnología. Dichos retos se centran en la búsqueda de catalizadores heterogéneos con alta actividad, comparable a la que presentan los catalizadores basados en sales de Fe^{2+} empleados en el proceso Fenton homogéneo, con alta eficiencia en el consumo de peróxido de hidrógeno, para minimizar el gasto derivado de este oxidante relativamente caro, y con buena estabilidad físico-química, que permita su operación en continuo. Bajo estas premisas se justifica el interés de la presente Tesis Doctoral que, permite, en el apartado de **Objetivos**, articular el objetivo general y los objetivos específicos de la investigación desarrollada.

El apartado de **Resultados y Discusión** es un compendio de contribuciones científicas, en su mayoría publicadas en revistas internacionales, como resultado del trabajo de investigación realizado durante el desarrollo de la presente Tesis Doctoral. Estos resultados se han clasificado en tres grandes bloques:

Bloque I, catalizadores de oro soportado sobre carbón activado para procesos de oxidación húmeda con peróxido de hidrógeno, dedicado al estudio sobre la aplicabilidad de nanopartículas de oro soportadas sobre carbón activado (Au/CA) como catalizador en procesos de oxidación húmeda con peróxido de hidrógeno. Este bloque consta de dos capítulos. El **Capítulo I** muestra los resultados obtenidos sobre el origen de la actividad de nanopartículas de oro soportadas atendiendo fundamentalmente a la influencia del tipo de soporte, del tamaño de partícula y de la naturaleza del contaminante. Este trabajo pone de manifiesto el potencial del catalizador Au/CA en el proceso objeto de estudio. El **Capítulo II** describe la influencia de las

variables de operación en la oxidación húmeda de fenol en presencia de Au/CA, así como la estabilidad y reusabilidad del mismo. A partir de estos resultados, y tras establecer la ruta de oxidación de fenol, se propone un esquema de reacción simplificado que permite, finalmente, obtener un modelo cinético para la descomposición de peróxido de hidrógeno y oxidación de fenol en presencia de dicho catalizador.

Capítulo I: Supported gold nanoparticle catalysts for wet peroxide oxidation. Applied catalysis B: Environmental 111-112 (2012) 81-89.

Capítulo II: Kinetics of wet peroxide oxidation of phenol over a gold/activated carbon catalyst. Submitted to Chemical Engineering Journal.

Bloque II, catalizadores basados en materiales carbonosos para procesos de oxidación húmeda con peróxido de hidrógeno, dedicado al estudio sobre la aplicabilidad de materiales carbonosos de diferente naturaleza, viz. carbones activados, negros de humos y grafitos, como catalizadores en procesos de oxidación húmeda con peróxido de hidrógeno. Este bloque lo constituyen tres capítulos. El Capítulo III da cuenta de la actividad de estos materiales en la reacción de descomposición de peróxido de hidrógeno a especies radicalarias, responsables de la oxidación de la materia orgánica disuelta en el agua. La originalidad de este trabajo se basa en la demostración de que la voltametría cíclica es una técnica sencilla, rápida, y concluyente para la predicción de la actividad catalítica de materiales carbonosos en esta reacción.

Una vez evaluada la actividad catalítica de estos materiales en la reacción de descomposición de peróxido de hidrógeno y, por tanto, confirmado su uso como cata-

lizadores en procesos de oxidación húmeda con este oxidante, se llevaron a cabo estudios dedicados al tratamiento de aguas residuales sintéticas, siendo fenol el compuesto elegido como contaminante modelo. Los resultados más relevantes obtenidos empleando carbones activados se recogen en el Capítulo IV, y los relativos al empleo de negros de humo y grafitos, en el Capítulo V. En ambos, además de evaluar la actividad catalítica de estos materiales, se analiza su eficiencia en el consumo de peróxido de hidrógeno y se estudia la estabilidad y reutilización de los mismos, aspectos clave para la viabilidad de los catalizadores heterogéneos en este tipo de procesos.

Capítulo III: The use of cyclic voltammetry to assess the activity of carbon materials for hydrogen peroxide decomposition. Carbon 60 (2013) 76-83.

Capítulo IV: Highly efficient application of activated carbon as catalyst for wet peroxide oxidation. Applied catalysis B: Environmental 140-141 (2013) 663-670.

Capítulo V: Graphite and carbon black materials as catalysts for wet peroxide oxidation. Applied catalysis B: Environmental 144 (2014) 599-606.

Bloque III, tratamiento de aguas residuales de la industria vitivinícola mediante oxidación húmeda con peróxido de hidrógeno con catalizadores basados en materiales carbonosos, constituido por el Capítulo VI, en el que demuestra el uso de determinados materiales carbonosos, seleccionados en los trabajos presentados en los capítulos anteriores, como catalizadores en el tratamiento de aguas procedentes de la industria vitivinícola mediante oxidación húmeda con peróxido de hidrógeno.

Capitulo VI: Treatment of high-strength winery wastewater by wet oxidation at mild temperature. Submitted to Separation & Purification Technology (2013).

Finalmente, las Conclusiones resumen las aportaciones originales de la Tesis Doctoral.

Completan este trabajo varios Apéndices.

El Apéndice I recopila los valores de referencia de los parámetros de contaminación de las aguas residuales, publicados en el Real Decreto 1620/2007.

El Apéndice II muestra una nomenclatura detallada de las abreviaturas empleadas a lo largo del trabajo.

El Apéndice III recoge las contribuciones a congresos como resultado de la investigación llevada a cabo en la presente Tesis Doctoral.

El Apéndice IV incluye otras publicaciones, como artículos y capítulos de libros, derivadas de la Tesis Doctoral y no recogidas en el apartado de Resultados y Discusión.

El Apéndice V incluye aquellas contribuciones a congresos cuyos resultados no han sido propiamente incluidos ni desarrollados en el presente documento.

2

Introducción

"El agua es un recurso natural escaso, indispensable para la vida y para el ejercicio de la inmensa mayoría de las actividades económicas; es irreemplazable, no ampliable por la mera voluntad del hombre, irregular en su forma de presentarse en el tiempo y en el espacio, fácilmente vulnerable y susceptible de usos sucesivos."

—Ley 25/1985, de 2 de agosto, de Aguas—

2.1 Problemática del agua

La abundancia de agua en la superficie de la Tierra es una característica única que distingue al "Planeta Azul" de otros en el Sistema Solar. Sin embargo, a pesar de que la mayor parte de la superficie del planeta esté cubierta por agua (72%), sólo una pequeña cantidad, que supone un 3% del total, es agua dulce y, por tanto, aprovechable. Dos terceras partes de este agua dulce se encuentran inmovilizadas en forma de glaciares, mientras que otra fracción importante la constituyen las aguas subterráneas, con lo que tan sólo el 1% se encuentra en la superficie terrestre en forma de ríos o almacenada en lagos y embalses. Es decir, que el agua es un recurso natural escaso por su origen. En la *Figura 2.1* se muestra, de forma detallada, la distribución de agua en el planeta Tierra.

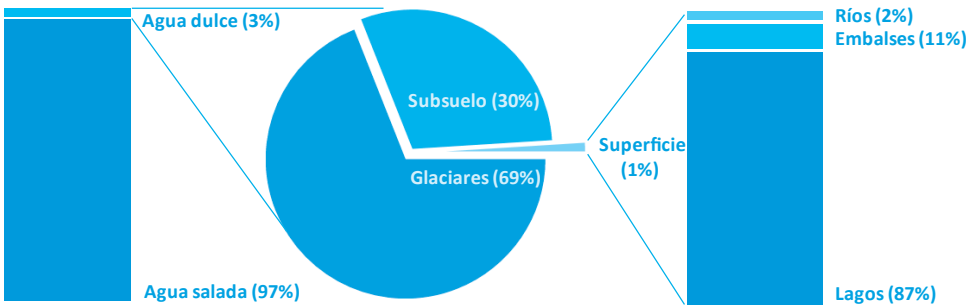

Figura 2.1. Distribución del agua en la Tierra (World Resources Institute, 1994)

Esta escasez se ve agravada por las enormes desigualdades en su disponibilidad en el espacio y el tiempo, por las variaciones de precipitación en las diferentes partes del mundo, el alto nivel de consumo desencadenado por el desarrollo demográfico e industrial, la consecuente reducción de recursos de agua de calidad como resultado de la contaminación, y en los últimos tiempos, por el efecto del calentamiento global, proceso que se prevé que originará graves problemas de sequía en amplias zonas del planeta *(Barceló, 2008)*.

Según la Organización Mundial de la Salud (OMS), más de mil millones de personas no tienen acceso al agua potable en la actualidad *(Barceló, 2008)* y la falta de acceso a agua limpia sigue siendo la primera causa de pérdida de esperanza de vida global. Desgraciadamente, el futuro no es esperanzador. La Organización de Naciones Unidas (ONU) predice que para 2050 más del 45% del mundo no podrá

contar con la porción mínima individual de agua para satisfacer las necesidades básicas.

Por otro lado, no sólo es de vital importancia la cantidad de agua disponible, sino también su calidad. El alto consumo de agua por parte del hombre en actividades industriales, agrícolas y domésticas, está dando lugar, cada vez en mayor medida, a elevados volúmenes de aguas residuales contaminadas *(United Nation Environment Programme, 2006)*. Todo ello ha hecho que el enfoque de la gestión hídrica se esté modificando en los últimos tiempos, considerando el problema de forma global. El objetivo es conseguir que la demanda de agua se ajuste a una oferta limitada, alcanzando un equilibrio entre ambas. Si el agua residual se limpia y purifica, se convierte en agua regenerada, que puede y debe ser utilizada de nuevo, regresando, de este modo, al punto inicial del ciclo. No se trata ya de buscar nuevas fuentes de agua, sino de recuperar la que se malgasta, regenerar la que se contamina y reutilizarla, especialmente en las actividades industriales *(Bayo y Angulo, 2009)*.

2.1.1 Aguas residuales industriales

El informe de la ONU sobre el desarrollo de los recursos hídricos del mundo, *El agua en un mundo en cambio (2009)*, apunta que el 70% del consumo total de agua se destina a consumo agrícola, el 20% a uso industrial y el 10% a gasto doméstico. En esta línea puede observarse una gran diferencia entre el mundo desarrollado y el que está en vías de desarrollo, tanto en la cantidad de agua consumida, como en la distribución que se hace de este recurso. Así, mientras que en Estados Unidos el consumo medio de agua es de 575 litros por persona y día, en Mozambique apenas llega a los 10 litros. Mientras que en los países

subdesarrollados la mayor parte de los recursos hídricos se consumen en el sector agrícola, en los desarrollados el 59% del consumo de agua se destina a uso industrial, correspondiendo a la agricultura y al gasto doméstico tan sólo un 30 y 11%, respectivamente.

En estos países, el sector industrial no sólo es el que más consume, sino también el que más contamina. Así, más de un 80% de los desechos peligrosos generados en el mundo se producen en los países industrializados, mientras que un 70% de los residuos generados en las naciones en vías de desarrollo se vierten al agua sin ningún tipo de tratamiento previo, contaminando así los recursos hídricos disponibles *(Rodríguez et al., 2009).*

En la *Directiva 91/271 CEE, del Tratamiento de Aguas Residuales Urbanas*, se definen los distintos tipos de aguas residuales:

- Aguas residuales domésticas: procedentes de viviendas y de servicios, generadas principalmente por el metabolismo humano y las actividades domésticas.
- Aguas residuales industriales: aguas residuales vertidas desde locales utilizados para efectuar cualquier actividad comercial o industrial, excluyendo las aguas residuales domésticas y las de escorrentía pluvial.
- Aguas urbanas: aguas residuales domésticas o la mezcla de las mismas con aguas residuales industriales y/o aguas de escorrentía pluvial.

Según los vertidos acuosos generados, las industrias pueden clasificarse en los siguientes grupos:

- Industrias con efluentes principalmente orgánicos: papeleras, azucareras, conserveras, mataderos, industrias de curtido, lavanderías, producción de alimentos, farmacéutica.
- Industrias con efluentes orgánicos e inorgánicos: refinerías y petroquímicas, coquerías, industria química de base, producción de fertilizantes e industria textil.
- Industrias con efluentes principalmente inorgánicos: industrias químicas de base, industrias de limpieza y recubrimiento de metales, explotaciones mineras y salinas.
- Industrias con efluentes con materia en suspensión: lavaderos de mineral y carbón, corte y pulido de minerales, laminación y colada.
- Industrias con efluentes de refrigeración: centrales de generación de energía eléctrica (térmicas y nucleares).

Cada una de ellas debe desarrollar y aplicar los métodos de tratamiento más adecuados para conseguir cumplir los requerimientos de vertido establecidos por la normativa pertinente.

2.1.2 Marco legal

El agua debe estar disponible no sólo en la cantidad necesaria, sino también con la calidad precisa en la forma que demanda la propia dinámica social. Como consecuencia de las actividades llevadas a cabo por el hombre se generan importantes volúmenes de agua contaminada. En este escenario, la regeneración y reutilización de dicho recurso es una necesidad que está dando lugar a una legislación cada vez más estricta en cuanto a límites de vertido.

La disposición de mayor relevancia de los últimos años ha sido la *Directiva 2000/60/CE del Parlamento Europeo y del Consejo*, de 23 de octubre de 2000, denominada *Directiva Marco del Agua*, por la que se establece un marco comunitario de actuación en el ámbito de la política de aguas. Esta Directiva persigue mejorar la protección de las aguas en sus aspectos cuantitativos y cualitativos, fomentar su uso sostenible y proteger los ecosistemas acuáticos, así como salvaguardar y desarrollar los usos potenciales de las aguas. Todo ello debe lograrse partiendo de la consideración primordial de que *"el agua no es un bien comercial como los demás sino un patrimonio que hay que proteger, defender y tratar como tal"*. Por ello, establece un marco para la protección de las aguas superficiales continentales, aguas de transición, aguas costeras y aguas subterráneas, de modo que se proteja y mejore el estado de los ecosistemas acuáticos, se reduzca progresivamente la contaminación del agua subterránea y se eviten nuevas fuentes de contaminación, se contribuya a paliar los efectos de las inundaciones y sequías y se promueva el uso sostenible del agua.

Como complemento a esta Directiva, se ha adoptado, a nivel europeo, la *Directiva 2006/118/CE*, de 12 de diciembre de 2006, relativa a la protección de las aguas subterráneas contra la contaminación y el deterioro, y se ha propuesto otra relativa a las normas de calidad ambiental en el ámbito de la política de aguas, por la que se modifica la *Directiva 2000/60/CE (COM(2006) 397 final)* y en la que se definen concentraciones máximas admisibles y medias anuales para las sustancias consideradas como prioritarias y otros contaminantes presentes en las aguas superficiales. Con fecha 16 de diciembre de 2008, se publica la *Directiva 2008/105/CE* del parlamento europeo y del consejo, relativa a las normas de calidad ambiental en el ámbito de la política de aguas, por la que se modifica la *Directiva 2000/60/CE*.

La Unión Europea fija los objetivos que se han de alcanzar, dejando en manos de las autoridades nacionales decidir en qué forma y con qué medios. La incorporación de la *Directiva Marco del Agua* a nivel estatal, se ha producido a través de distintos instrumentos normativos. La *Ley 62/2003*, de 30 de diciembre, de medidas fiscales, administrativas y del orden social, con su artículo 129 modificó el *Real Decreto Legislativo 1/2001*, de 20 de julio, por el cual se aprobaba el texto refundido de la *Ley de Aguas*, que constituye el principal pilar sobre el que se asienta todo el régimen legal español en materia de contaminación de aguas. El *Real Decreto-Ley 4/2007*, de 13 de abril, modifica el texto refundido de la *Ley de Aguas*. Por otro lado, el ámbito territorial de las Demarcaciones Hidrográficas correspondientes a cuencas intercomunitarias e internacionales se ha fijado mediante el *Real Decreto 125/2007*, de 2 de febrero y, las autoridades competentes, se han regulado en el *Real Decreto 126/2007*, de 2 de febrero. La última medida legislativa adoptada por el Estado español en cumplimiento de la *Directiva 2000/60/CE* ha sido el *Real Decreto 907/2007*, de 6 de julio, por el cual se aprueba el Reglamento de la Planificación Hidrológica.

Como complemento a la *Directiva Marco del Agua* también se ha adoptado, a nivel español, el *Real Decreto 140/2003*, de 7 de febrero, en el cual se establecen los criterios sanitarios de la calidad del agua de consumo humano, que deroga el anterior *Real Decreto 1138/1990*, de 14 de septiembre, por el que se trasladaba la *Directiva comunitaria 80/778/CEE*, de 15 de julio de 1980, y con el cual queda incorporada al ordenamiento jurídico español la *Directiva comunitaria 98/83/CE*.

El *Real Decreto 1620/2007*, de 7 de diciembre, establece el régimen jurídico de la reutilización de las aguas depuradas, mientras que en la *Orden MAM/85/2008*,

de 16 de enero, se establecen los criterios técnicos para la valoración de los daños al dominio público hidráulico, y las normas sobre toma de muestras y análisis de vertidos de aguas residuales. Estas dos disposiciones contienen las sustancias peligrosas contempladas en la *Directiva Marco del Agua* y se incluyen valores de referencia de los parámetros de contaminación (sustancias peligrosas, contaminantes y otros contaminantes, recogidas en el **Apéndice I**), estableciendo estimaciones generales de normas de calidad ambiental y objetivos de calidad. A través de el *Real Decreto 1290/2012,* de 7 de septiembre, se establecen las normas aplicables al tratamiento de las aguas residuales urbanas, mediante la incorporación de nuevos contenidos en los planes hidrológicos de cuenca, relacionados, en su mayor parte, con la protección, conservación y mejora del estado de las masas de agua y del dominio público hidráulico y, por tanto, con la utilización y protección de éste.

En cuanto al tratamiento de aguas residuales urbanas, la *Directiva 91/271/CEE*, de 21 de mayo de 1991, establece las medidas necesarias que los Estados miembros han de adoptar para garantizar que las aguas residuales urbanas reciben un tratamiento adecuado antes de su vertido. De forma resumida, la Directiva establece dos obligaciones claramente diferenciadas, en primer lugar las "aglomeraciones urbanas" deberán disponer de sistemas colectores para la recogida y conducción de las aguas residuales y, en segundo lugar, se prevén distintos tratamientos a los que deberán someterse dichas aguas antes de su vertido a las aguas continentales o marinas, de modo que se garantice la ausencia de efectos nocivos sobre las personas y el medio ambiente. La tendencia, por tanto, a nivel europeo y estatal, especialmente tras la promulgación de la *Ley 16/2002*, de prevención y control integrados de la contaminación, y la puesta en marcha del *PRTR-España (Registro Estatal de Emisiones y Fuentes Contaminantes)*, es reducir el vertido de algunos

contaminantes específicos y emplear sistemas avanzados de tratamiento de aguas residuales *in situ*. Esta ley recoge una lista de las principales sustancias contaminantes para las que han de fijarse valores límite de emisiones a las aguas, teniendo en cuenta las mejores técnicas disponibles, las características técnicas de la instalación y su localización geográfica:

- Compuestos órgano-halogenados y sustancias que puedan dar origen a compuestos de esta clase en el medio acuático.
- Compuestos organofosforados.
- Compuestos organoestánicos.
- Sustancias y preparados cuyas propiedades cancerígenas, mutágenas o que puedan afectar a la reproducción en el medio acuático.
- Hidrocarburos persistentes y sustancias orgánicas tóxicas persistentes y bioacumulables.
- Cianuros.
- Metales y sus compuestos.
- Arsénico y sus compuestos.
- Biocidas y productos fitosanitarios.
- Materias en suspensión.
- Sustancias que contribuyen a la eutrofización (en particular nitratos y fosfatos).
- Sustancias que ejercen una influencia desfavorable sobre el balance de oxígeno (y computables mediante parámetros tales como la DBO y DQO)

2.2 Tratamientos de aguas residuales industriales

Las aguas residuales urbanas son recogidas mediante un sistema colector y enviadas a estaciones depuradoras de aguas residuales (EDAR). Las industrias que realicen el vertido de sus aguas residuales en estas estaciones habrán de acondicionarlas previamente. Las EDAR disponen de distintas etapas, comenzando por PRETRATAMIENTOS FÍSICOS, en los que se separan los sólidos de mayor tamaño y las grasas (desbaste, desarenado y desengrasado); TRATAMIENTOS PRIMARIOS, basados en la coagulación y floculación de la materia en suspensión para su posterior decantación; TRATAMIENTOS BIOLÓGICOS O SECUNDARIOS, donde se engloban todos los procesos de digestión aerobia o anaerobia de la materia orgánica del efluente y, finalmente, en las ocasiones que lo requieran, TRATAMIENTOS TERCIARIOS, que tienen como objetivo la eliminación de las sustancias específicas que permanecen en el agua residual tras los procesos convencionales anteriores; se trata pues, de tratamientos avanzados.

En la *Figura 2.2* se muestra el esquema de una EDAR convencional, atendiendo tanto a la línea de aguas como a la de los fangos producidos en las diversas etapas de tratamiento.

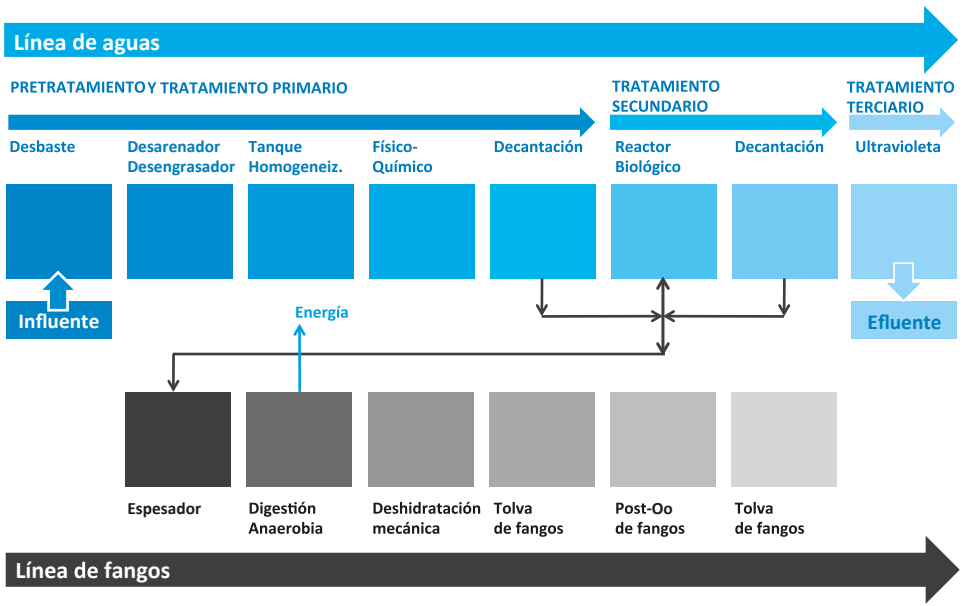

Figura 2.2. Esquema de una estación de agua residual (EDAR).

Dada la heterogeneidad de las actividades industriales, las aguas residuales generadas se caracterizan por presentar una composición y un caudal muy variable dependiendo del tipo de industria y de los ciclos de producción de la misma, con lo que las fluctuaciones del caudal de vertido son impredecibles. De este modo, aunque los vertidos industriales producen, generalmente, un menor volumen de agua residual que los urbanos, sus características provocan efectos más dañinos, ya que, en ocasiones se trata de vertidos con componentes tóxicos y/o bioacumulables, lo

que impide su tratamiento en una EDAR convencional. Todo ello hace que estas aguas residuales industriales requieran un tratamiento previo hasta disminuir la concentración de contaminantes a un nivel asimilable por la estación depuradora *(Rodríguez et al., 2009)*. Éste es el caso de multitud de compuestos presentes en las aguas residuales industriales: compuestos amoniacales (procedentes de la producción de fertilizantes, explosivos y fármacos), cianuros (metalurgia, síntesis orgánica), hidrocarburos halogenados (pesticidas, disolventes, polímeros), surfactantes (detergentes, metalurgia, extracción) y compuestos fenólicos (resinas, nylon, industria papelera, petroquímica, gasificación del carbón).

Los sistemas de depuración de aguas residuales industriales tratan de devolver el agua al medio natural con unas características físicas, químicas y biológicas lo más parecidas a su estado natural. El nivel máximo admisible de contaminante puede conseguirse mediante la utilización de diversas técnicas (solas o acopladas entre sí) destructivas y no destructivas. La ***Tabla 2.1*** recoge los métodos de tratamientos de aguas residuales industriales más habituales.

Los métodos no destructivos suponen la transferencia del contaminante del agua residual a otro medio; suelen usarse como una etapa previa de concentración del contaminante antes de abordar su destrucción química. Por su parte, los tratamientos destructivos implican la transformación del contaminante en otros productos inocuos o de menor toxicidad.

Tabla 2.1. Métodos de tratamiento de aguas residuales industriales.

MÉTODOS DE TRATAMIENTOS DE AGUAS RESIDUALES INDUSTRIALES		
No destructivos	**Destructivos**	
Adsorción	**Reducción**	
	Oxidación biológica	
Desorción	**Oxidación química**	Incineración
Extracción con disolventes		Oxidación húmeda supercrítica
Tecnología de membranas		Oxidación húmeda catalítica y no catalítica con aire
		Procesos de oxidación avanzada

La aplicación de un método u otro depende, fundamentalmente, de la naturaleza del contaminante y del caudal de agua a tratar. Al mismo tiempo, debe ser un proceso medioambientalmente aceptable y a un coste razonable. En la *Figura 2.3* se muestran los intervalos de aplicación más habituales de los procesos de tratamiento de aguas residuales industriales contaminadas por compuestos orgánicos en función de la concentración de contaminante, expresada como demanda química de oxígeno (DQO), y del caudal de agua a tratar.

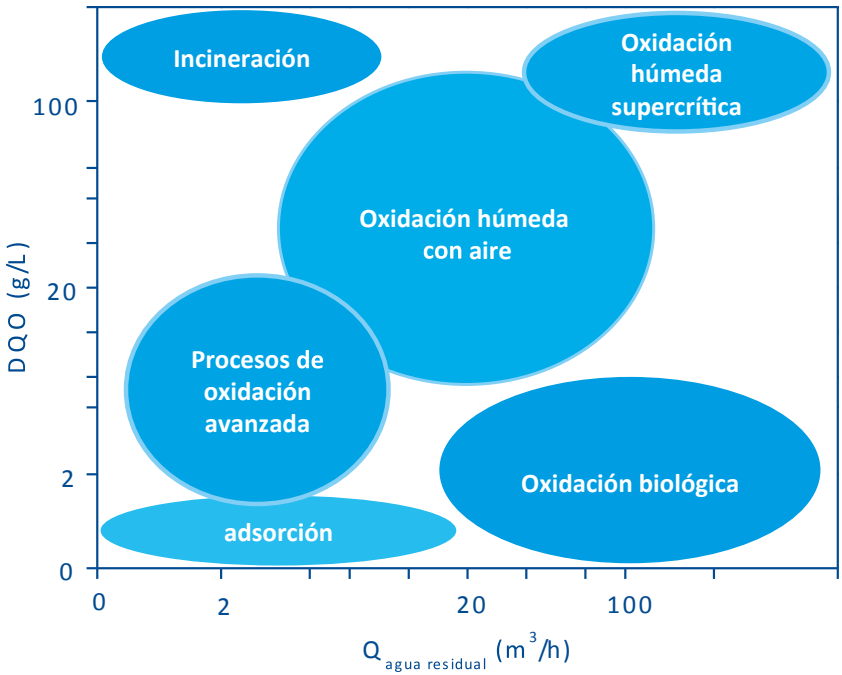

Figura 2.3 Intervalos de aplicación de diferentes procesos de tratamiento de aguas residuales con contaminantes orgánicos (parcialmente modificado de Hancock, 1999).

2.2.1 Tratamientos no destructivos

Dentro de los tratamientos no destructivos, destacan el proceso de adsorción, la desorción o *stripping*, la extracción con disolventes y la tecnología de membranas.

La adsorción física consiste en la captación de sustancias solubles en la superficie de un sólido adsorbente, por lo que la superficie específica de éste representa un parámetro fundamental. De ahí, que los carbones activados, gracias a su elevado desarrollo superficial (S_{BET}≈1000-2000 m^2/g), sean los adsorbentes más empleados *(Sanghi y Bhattacharya., 2002)*. Otros materiales utilizados son las arcillas *(Çelik et al., 2000)*, zeolitas *(Wang y Peng, 2010)*, resinas poliméricas *(Lin y Juang, 2009)*, MOFs *(Khan et al., 2012)*, etc. Esta técnica es empleada, fundamentalmente, para retener contaminantes de naturaleza orgánica (colorantes, fenol, mercaptanos, etc.) *(Rodríguez et al., 2009)* presentes en corrientes acuosas relativamente diluidas (DQO<1 g/L), por lo que, en muchas ocasiones, se utiliza como etapa final tras otros sistemas de tratamiento; generalmente, tras un proceso biológico. La operación es menos efectiva en el caso sustancias de pequeño tamaño molecular y estructura sencilla; no obstante, éstas suelen ser fácilmente biodegradables, por lo que es preferible su tratamiento mediante oxidación biológica. La adsorción presenta serios inconvenientes desde el punto de vista de los residuos generados, por lo que la viabilidad económica del proceso radica en la posibilidad de la regeneración y reutilización del adsorbente.

La desorción o *stripping* consiste en el arrastre de compuestos orgánicos volátiles disueltos en las aguas mediante una corriente gaseosa (aire o vapor de agua). Se trata de un proceso aplicado a escala industrial, apto para grandes cantidades de efluente. Ha sido ampliamente utilizado para la eliminación de compuestos orgánicos volátiles disueltos (*i.e.* hidrocarburos clorados, amoniaco, sulfuro de hidrógeno, disolventes orgánicos, gasolina, gasóleo, compuestos aromáticos, mercaptanos, fenol, etc.) en aguas residuales industriales *(Qi et al., 2011)*, potabilización de aguas y tratamiento de aguas subterráneas *(Linek et al., 1998)*. Es especialmente adecuado

para bajas concentraciones de contaminante. Presenta el inconveniente de generar una corriente gaseosa residual contaminada, que debe tratarse antes de su emisión a la atmósfera *(Hidalgo et al., 2004)*.

La extracción de contaminantes orgánicos con disolventes en fase líquida es un método económico y relativamente eficaz cuando la concentración del compuesto a extraer o su precio es elevado *(Greminger et al., 1982)*. Esta tecnología ha sido ampliamente empleada para el tratamiento de aguas contaminadas con diversos compuestos orgánicos, entre los que destaca el fenol, para el que se alcanza un porcentaje de recuperación superior al 99% *(Jiang et al., 2003)*. El principal inconveniente de esta tecnología radica en la pérdida de disolventes (***i.e.*** alcoholes, aminas, ácidos orgánicos) por su transferencia al agua, lo que puede crear un problema de contaminación adicional *(Bravo et al., 2004)*.

La tecnología de membranas consiste en la utilización de barreras físicas semipermeables que separan dos fases, impidiendo su íntimo contacto y restringiendo selectivamente el movimiento de las moléculas a través de ellas. De este modo se consigue la separación de los contaminantes del agua, generando un efluente acuoso depurado y otro concentrado en el contaminante. Incluye diversas variantes: microfiltración (MF) *(Hilal et al., 2005, Park et al., 2012)*, ultrafiltración (UF) *(Hilal et al., 2005)*, nanofiltración (NF) *(Hilal et al., 2004)*, ósmosis inversa (OI) *(Gaid y Treal, 2007)*, electrodiálisis reversa (EDR) *(Hsu et al., 2012)* y electrodesionización (EDI) *(Lu et al., 2010)*. Estas técnicas son aplicables generalmente al caso de efluentes acuosos con baja concentración de contaminantes, por lo que suelen emplearse combinadas con otros tratamientos. Los efluentes tratados mediante la tecnología de membranas son muy diversos: aguas resi-

duales de destilerías *(Prodanović y Vasić, 2013)*, industria farmacéutica *(Park et al., 2004)*, aguas residuales municipales *(Ke et al., 2013)*, pesticidas *(Plakas y Karabelas, 2012)*, etc. El principal problema de esta tecnología radica en las altas presiones necesarias (hasta 70 bares) y en el ensuciamiento de las membranas debido a la presencia de diversas sustancias en la alimentación que pueden interaccionar con ella (adsorbiéndose y/o precipitando en su superficie o penetrando en su interior). La investigación en esta área está enfocada en la mejora de materiales para solucionar los problemas de ensuciamiento, mejorar los caudales de permeado y abaratar los costes. Entre los procesos existentes, la nanofiltración *(Zahoor y Mahramanlioglu, 2011)* y la ósmosis inversa *(Williams et al., 1999)* son los que presentan mayor grado de aplicación industrial para el tratamiento de aguas residuales.

2.2.2 Tratamientos destructivos

Los tratamientos destructivos pueden dividirse a su vez en tratamientos químicos de reducción y de oxidación.

Los tratamientos de reducción más empleados para la eliminación de contaminantes orgánicos en aguas residuales industriales son los que emplean hidrógeno como agente reductor; normalmente a presión y temperatura moderadas, en presencia de un catalizador. Otros reductores empleados son hidruros metálicos, ácido fórmico, hidracina y alcóxidos *(Monsalvo, 2010)*. Mediante los tratamientos de reducción, a diferencia de los de oxidación, no se consigue reducir el contenido en materia orgánica, por lo que tienen que ser concebidos únicamente como un pretratamiento.

El tratamiento de reducción más utilizado es la **hidrodecloración catalítica**. Éste consiste en la ruptura del enlace cloro-carbono de una molécula orgánica clorada mediante su hidrogenación, generando el correspondiente compuesto orgánico sin cloro, el cual es eliminado como HCl. Este tratamiento es muy eficiente para la transformación de los compuestos orgánicos clorados en otros menos tóxicos o inocuos, que puedan ser eliminados posteriormente, con mayor facilidad, mediante otros tratamientos *(Matatov-Meital y Sheintuch, 1998)*. Esta tecnología fue aplicada a escala de planta piloto por *Kalnes y James (1988)* y *Brinkman et al. (1995)* para el tratamiento de productos clorados generados en la industria petroquímica y de los residuos procedentes del tratamiento de destilación de una corriente orgánica de ácido sulfúrico, respectivamente.

Los tratamientos de oxidación biológica son los métodos de tratamiento de aguas residuales más económicos *(Padilla et al., 2005)*. Los contaminantes son transformados o eliminados gracias a la acción de microorganismos en presencia de oxígeno, que los metabolizan y adsorben en su interior. Una ventaja de estos procesos frente al resto de tratamientos es su versatilidad, tanto en el caudal de agua a tratar como en la diversidad y concentración de materia orgánica que pueden soportar. Como desventaja, se genera una importante cantidad de fangos como consecuencia del elevado crecimiento bacteriano. Su aplicación está condicionada por la baja solubilidad del oxígeno en el agua *(Rodríguez et al., 2009)*. Existen varios procesos biológicos aerobios para el tratamiento de aguas residuales contaminadas con compuestos orgánicos; entre ellos destacan los LODOS ACTIVOS, los REACTORES SECUENCIALES DE FLUJO DISCONTINUO (SBR), los REACTORES BIOLÓGICOS DE MEMBRANA (MBR) y los REACTORES BIOLÓGICOS ROTATIVOS (RBC).

Los sistemas de oxidación aerobia convencionales, instalados en las EDAR ***(Figura 2.2)*** son los LODOS O FANGOS ACTIVOS. Éstos consisten en el desarrollo de un cultivo bacteriano disperso en forma de flóculo en un depósito agitado, aereado y alimentado con el agua residual, que es capaz de metabolizar como nutrientes los contaminantes orgánicos presentes en el agua *(Ronzano y Dapena, 1995)*. Un importante inconveniente asociado a este proceso es la generación de lodos, que hace necesaria su separación mediante decantación y su gestión como residuo. Actualmente, la investigación está centrada en el desarrollo de otro tipo de reactores aerobios de carácter más modular que, además, permiten el tratamiento de compuestos refractarios a los sistemas biológicos convencionales, como los SBR. Así, se han descrito aplicaciones con éxito para aguas residuales municipales, aguas procedentes de la industria vitivinícola y destilerías, lixiviados de vertederos, industrias de curtidos, industria papelera, industria láctea y aguas residuales de matadero, entre otras *(Aguado, 2006)*. La principal desventaja frente al tratamiento mediante lodos activos convencional es que se trata de un sistema más complejo, por lo que precisa de un mayor mantenimiento *(Vargas et al., 2000)*. Además, la gestión de los lodos residuales sigue siendo necesaria. En este sentido, destacan los reactores de membrana (MBR y RBC), que han conseguido eliminar los problemas asociados a la sedimentación de los lodos. Además, estos reactores son más versátiles que los procesos de fangos activos en cuanto al caudal y concentración de materia orgánica a tratar, y presentan una mayor resistencia frente a la presencia puntual de compuestos tóxicos en el agua de alimentación. Las recientes innovaciones técnológicas y reducciones de costes están conduciendo a un aumento en la aplicación de la tecnología MBR al tratamiento de aguas residuales, tanto municipales *(Krzeminski et al., 2012, Cartagena et al., 2013)* como industriales *(Hussain et al., 2010, Beier et al., 2012)*. Por su parte, los reactores tipo RBC han sido empleados para el

tratamiento de aguas residuales municipales *(Yun-lu et al., 2012)*, aguas residuales de la industria petrolífera *(Chavan y Mukherji, 2010)* y de la industria alimentaria *(Najafpour et al., 2006)* entre otras; sin embargo, su aplicación a nivel industrial está limitada, ya que el elevado consumo energético derivado del sistema de giro de esta tecnología, los hace inviables para tratar caudales elevados *(Cortez et al., 2008, Rodríguez et al., 2009)*.

Los tratamientos de oxidación química consisten en la transformación de la materia orgánica disuelta en el agua mediante la adición de un agente oxidante (*i.e.* oxígeno, ozono, peróxido de hidrógeno, etc.). Entre los tratamientos de oxidación química destacan la incineración, la oxidación húmeda supercrítica, la oxidación húmeda con aire y los procesos de oxidación avanzada.

El proceso de **incineración** es una técnica convencional empleada para el tratamiento de aguas residuales con elevada carga, que consiste en la combustión completa de la materia orgánica o inorgánica con aire hasta su conversión en cenizas, a presión atmosférica y un rango de temperatura entre 730 y 1200 °C (o por debajo de este rango cuando se emplean catalizadores). La incineración de un agua residual sólo es autosostenible si la carga orgánica de ésta es suficiente para asegurar un soporte energético adecuado para el calentamiento y la vaporización del agua (DQO>50 g/L). En caso contrario, la planta de incineración debe operar con combustible de apoyo, con lo que los costes de operación se vuelven excesivos. Estas aguas suelen contener compuestos que no son fácilmente biodegradables o que pueden perturbar el proceso biológico en una EDAR, o con propiedades demasiado nocivas para ser emitidos a un sistema de alcantarillado ordinario. La eficacia de esta tecnología en la eliminación de carbón orgánico total

(COT) ronda el 99% *(Ministerio de Medio Ambiente y Medio Rural y Marino, 2009)*. Los productos de reacción son dióxido de carbono, agua y otros compuestos inorgánicos (óxidos de nitrógeno, óxidos de azufre, haluros de hidrógeno, fosfatos, compuestos de metales pesados) que varían en función de los contaminantes presentes en las aguas a tratar *(Ministerio de Medio Ambiente y Medio Rural y Marino, 2009)*. Además, es muy común la generación de dioxinas y furanos, compuestos altamente tóxicos, por lo que se trata de un método de eliminación de residuos controvertido. A nivel industrial existen varios ejemplos de unidades de incineración de aguas residuales, como la que se encuentra en las instalaciones de Repsol Química S.A., ubicada en el término municipal de Puertollano (Ciudad Real), para el tratamiento de corrientes fenólicas procedentes de las plantas de estireno y polioles.

La **oxidación húmeda supercrítica** (*Supercritical Wet Oxidation, SCWO*) se basa en la oxidación de los contaminantes orgánicos en las condiciones supercríticas del agua (374 °C, 221 atm), o por encima de éstas; usualmente alrededor de 650 °C y 250 atm *(Yu y Savage, 2000)*. El proceso es económicamente competitivo para el tratamiento de aguas con concentraciones de materia orgánica elevadas ***(Figura 2.3)***, de forma que se favorezca la autosostenibilidad térmica de la reacción. La oxidación húmeda supercrítica se aplica a contaminantes con baja biodegradabilidad y/o elevada toxicidad en la industria química, petroquímica y farmacéutica, lodos industriales y municipales, dioxinas y PCBs (bifenilos policlorados) *(Ministerio de Medio Ambiente y Medio Rural y Marino, 2009)*. Los grados de eliminación alcanzados mediante este proceso son superiores al 99,9% para la mayor parte de los compuestos orgánicos (el carbono orgánico se convierte en CO_2, el nitrógeno en N_2, los halógenos se convierten a su ácido

correspondiente, mientras que el azufre en H_2SO_4), y los tiempos de reacción se encuentran entre los 30 y 60 segundos, en función de la temperatura de reacción *(Ministerio de Medio Ambiente y Medio Rural y Marino, 2009)*. Por lo tanto, la principal ventaja de esta tecnología frente a otros procesos de oxidación química, como la oxidación húmeda y los procesos de oxidación avanzada, es que alcanza la mineralización (oxidación completa a CO_2 y H_2O) de los contaminantes en un tiempo de residencia menor *(Modell, 1989)*.

Por otro lado, los principales inconvenientes asociados a esta tecnología son la precipitación de los sólidos inorgánicos como sales, lo que puede dar lugar a importantes problemas de corrosión, junto con los elevados costes de inversión y de operación derivados de trabajar a tan alta presión y temperatura. Como consecuencia de estas dificultades, los procesos de oxidación húmeda supercrítica se encuentran todavía en fase de investigación *(Rodríguez et al., 2009)*. El proceso **SUWOX** (*Supercritical Water Oxidation*) constituye uno de los últimos desarrollos encaminados a superar los problemas asociados a la corrosión y deposición de sales, inherentes a esta tecnología. Ha sido ensayado a escala semiindustrial para el tratamiento de aguas residuales de la industria farmacéutica y aguas contaminadas con biocidas *(http://hdl.handle.net)*.

La oxidación húmeda con aire (*Wet Air Oxidation, WAO*) es un proceso de oxidación de la materia orgánica disuelta en el agua empleando una fuente de oxígeno en fase gas, normalmente aire u oxígeno molecular, a altas temperaturas (200–374 °C) y presiones (5-200 atm), pero siempre inferiores a las condiciones críticas del agua. El poder oxidante de este sistema se explica atendiendo a las condiciones de operación empleadas; las altas temperaturas aumentan la velocidad de

reacción y la producción de radicales libres (mecanismo por el cual tiene lugar la oxidación), mientras que las altas presiones aumentan la concentración del oxígeno disuelto *(Mishra et al., 1995, Kolaczkowski et al., 1999)*. Este proceso es empleado para el tratamiento de aguas residuales con concentraciones de materia orgánica elevadas (DQO entre 20 y 200 g/L) *(Mantzavinos et al., 1999)*. En estas condiciones, el proceso es autotérmico, de modo que el propio calor de reacción hace que la temperatura del reactor se eleve hasta el valor deseado para llevar a cabo la oxidación, sin necesidad de realizar un aporte externo de energía para mantener la temperatura de operación.

En ocasiones, aunque la concentración de materia orgánica sea inferior, o los productos parcialmente biodegradables, la oxidación húmeda con aire puede sustituir a una EDAR biológica si la cantidad de agua residual es demasiado pequeña para justificar una planta de este tipo o si no hay tratamiento biológico disponible *(Ministerio de Medio Ambiente y Medio Rural y Marino, 2009)*.

La primera planta de oxidación húmeda comercial fue desarrollada por la empresa **Zimpro Inc**., a principios de los años 30, para el tratamiento y recuperación de materias primas de los efluentes de plantas papeleras. En la ***Figura 2.4*** se muestra un esquema simplificado de dicho proceso. En la década de los sesenta, se comenzó a aplicar para el tratamiento de lodos biológicos de depuradora. A partir de los años setenta, la aplicación de la oxidación húmeda con aire se centró en el tratamiento de efluentes industriales. En la actualidad, existen en el mundo más de un centenar de plantas en operación, la mayoría de las cuales tratan aguas residuales procedentes de la industria química, petroquímica y farmacéutica, entre otras *(Rodríguez et al., 2009)*.

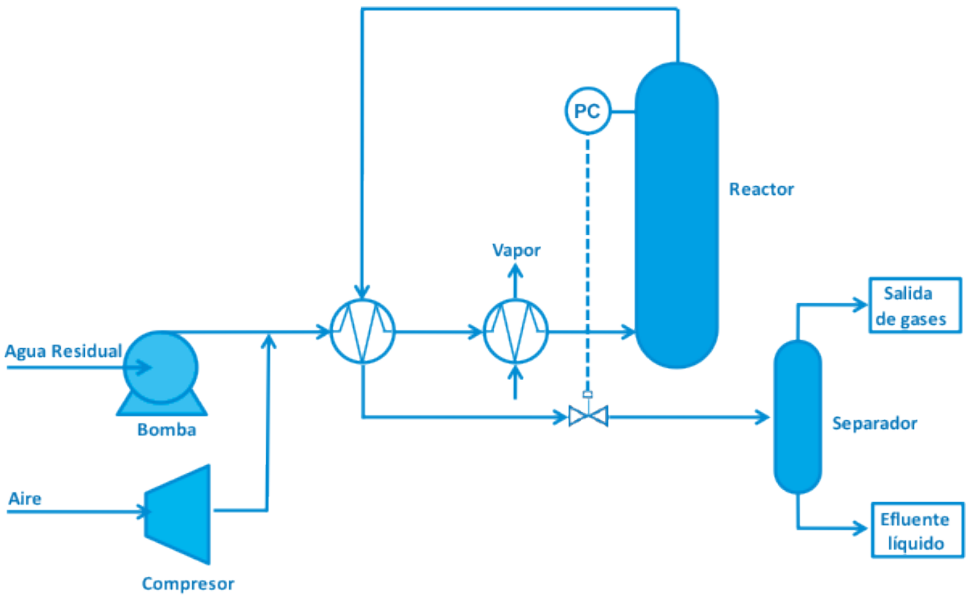

Figura 2.4. Esquema simplificado de una unidad de oxidación húmeda con aire (tecnología ZIMPRO) (http://www. Zimpro_Wet_Air_Oxidation.aspx)

Las sustancias o contaminantes preferiblemente considerados para su tratamiento mediante esta tecnología son los derivados fenólicos y nafténicos, compuestos aromáticos clorados, compuestos aromáticos nitrogenados, compuestos organosulfurados, organofosforados, organoclorados, nitritos y sulfitos *(Ministerio de Medio*

Ambiente y Medio Rural y Marino, 2009). Mediante la oxidación húmeda con aire se obtienen elevadas conversiones de los contaminantes orgánicos (>90%) y una reducción de la demanda química de oxígeno entre el 60-90% con tiempos de residencia entre 10 y 120 minutos *(Quintanilla et al., 2012)*. Rara vez es posible alcanzar la mineralización completa de los efluentes debido a la formación de ácidos carboxílicos (*i.e.* ácido acético, fórmico y propiónico, entre otros), subproductos de la reacción, refractarios al tratamiento de oxidación a las condiciones de presión y temperatura empleadas *(Levec y Pintar, 2007, Rodríguez et al., 2009)*. Puesto que éstos son compuestos biodegradables, una opción interesante es emplear esta tecnología acoplada a un tratamiento biológico posterior.

El principal inconveniente de la oxidación húmeda es el elevado coste de inversión, debido, fundamentalmente, a los materiales de construcción, que deben ser los adecuados para soportar las altas temperaturas y presiones, y evitar problemas de corrosión. Los principales esfuerzos se han centrado en reducir el capital de inversión y, por tanto, en suavizar las condiciones de operación (temperatura y presión), manteniendo una velocidad de transferencia de materia adecuada y una velocidad de reacción elevada. Con este fin, se han estudiado diversos aspectos, como el contacto entre los reactivos, el régimen de flujo hidrodinámico, y la incorporación de catalizadores, siendo este último el más prometedor.

La oxidación húmeda catalítica con aire (*Catalytic Wet Air Oxidation, CWAO*) empezó a desarrollarse también en la década de los 50, cuando Dupont registra la primera patente de un catalizador de óxido de manganeso, cromo y zinc. A partir de ese momento se investigó en tecnologías que emplearan catalizadores homogéneos y heterogéneos. En la *Tabla 2.2* se resumen los procesos de oxidación húmeda

catalítica con aire comerciales existentes, y se recogen aspectos como el tipo de reactor, las condiciones de operación, los tiempos de residencia y los catalizadores empleados. Los procesos de mayor implantación industrial son los que emplean catalizadores homogéneos, principalmente sales de cobre. Éstos proporcionan altos grados de oxidación, pero conllevan la existencia de una etapa adicional de separación y recuperación del mismo, con el consecuente encarecimiento del tratamiento. Los procesos comerciales basados en catálisis heterogénea (**Kurita**, **NS-LC**, **Osaka Gas**) se desarrollaron fundamentalmente en Japón. En ellos se emplean metales preciosos o metales de transición soportados sobre óxidos de titanio y circonio. La investigación actual en este campo está orientada a la búsqueda de catalizadores heterogéneos estables *(Quintanilla et al., 2012)*. Los óxidos de metales (Cu, Mn, Co, Zn, Ce y Bi) exhiben una actividad adecuada, pero tienen una vida muy limitada debido a la lixiviación de la fase activa. Los metales nobles soportados (Ru, Pt, Pd, Ir, Ag y Rh) son los más estudiados por su elevada actividad y alta resistencia a la lixiviación, pero tienen un coste excesivamente elevado y presentan problemas de envenenamiento por depósitos carbonosos *(Matatov-Meytal y Sheintuch, 1998, Imamura, 1999)*.

Por su parte, algunos materiales carbonosos, como carbones activados, grafitos y negros de humo, han sido estudiados como soportes catalíticos o catalizadores de este proceso *(Stüber et al., 2005, Gomes et al., 2008, Yang et al., 2008)*, mostrando actividades más modestas en el caso de no incorporar fase activa metálica. La tendencia actual en los procesos CWAO se centra en el campo de los nanomateriales. Entre los más estudiados se encuentran las nanoestructuras carbonosas *(Gomes et al., 2004, Yang et al., 2008, Rodríguez et al., 2008)* como nanotubos, nanofibras y xerogeles, y las nanopartículas de oro *(Besson y Gallezot, 2003, Milone et al., 2006)*.

Tabla 2.2. Reactores, condiciones de operación, tiempos de residencia y catalizadores en procesos comerciales CWAO (Quintanilla et al., 2012).

Unidad comercial	Reactor	T (K)	P (MPa)	tr (h)	Catalizador
Loprox	Columna de burbujeo	313-473	0,5-2	1-3	Fe^{2+} y H_2O_2 (promotor)
IT Enviroscience	Tanque agitado	438-548	1,2-7	0,5-2	Br^-, NO^{3-}, Mg^{2+}
Ciba-Geigy	Columna de burbujeo	573	20	3	Cu^{2+}
Orcan	-	120	0,3	-	Fe^{2+} y H_2O_2 (promotor)
Kurita	-	170	-	-	Pd soportado
ATHOS	-	235	4	-	Cu^{2+}
NS-LC	Lecho de goteo	433-543	0,9-8	1	Pt-Pd/TiO_2-ZrO_2 (monolitos), Ru/CeO_2 (*pellets*)
Osaka Gas	Lecho de goteo	523	7	0.5	Fe, Cu, Co o Ni/ Ru, Pd, Pt o Au/TiO_2 o ZrO_2

Una variante de este proceso lo constituye la **oxidación húmeda catalítica promovida por peróxido de hidrógeno** (*Promoted-Hydrogen Peroxide Catalytic Wet Air Oxidation, PP-CWAO*), en la cual se añaden pequeñas cantidades de peróxido de hidrógeno (porcentajes en torno al 10% de la cantidad estequiométrica necesaria

para mineralizar la materia orgánica presente) para iniciar o promover las reacciones radicalarias de oxidación. De este modo se consigue una importante reducción en los tiempos de residencia y se abaratan los costes. A nivel industrial existen ejemplos de la aplicación de esta tecnología, como los procesos **Loprox** y **ATHOS**, recogidos en la ***Tabla 2.2***. Recientemente, se ha demostrado el efecto beneficioso del peróxido de hidrógeno como promotor de radicales libres, combinado con el oxígeno, cuando se emplean carbones activados como catalizadores del proceso *(Rubalcaba et al., 2007, Quintanilla et al., 2010)*.

Los **procesos de oxidación avanzada** (*Advanced Oxidation Processes, AOPs*) fueron definidos por *Glaze et al. (1987)* como *"aquellos procesos y tratamientos de aguas a presión y temperatura cercanas a las condiciones ambientales, que implican la generación de radicales hidroxilo en cantidad suficiente para interaccionar con los compuestos orgánicos del medio"*. Sin embargo, esta definición ha quedado obsoleta; englobando, actualmente, los procesos de oxidación avanzada, todos aquellos procesos en los que la materia orgánica es oxidada por especies radicalarias, radicales hidroxilo (·OH) e hidroperóxido (·OOH), en condiciones relativamente suaves de presión y temperatura (T=25-130 °C, P=1-5 atm).

2.3 Procesos de oxidación avanzada

Los procesos de oxidación avanzada involucran la generación y uso de especies transitorias con un alto potencial oxidante, como el radical hidroxilo (·OH) y el hidroperóxido (·OOH). El radical hidroxilo presenta una elevada efectividad en la degradación de la materia orgánica y, gracias a su alto poder oxidante *(Tabla 2.3)*, reacciona con ella de forma no selectiva y a velocidades muy superiores a las que lo hacen otras especies oxidantes comúnmente empleadas, como, por ejemplo, el oxígeno. En la *Tabla 2.3* se recoge el potencial de oxidación de las principales especies oxidantes.

Tabla 2.3 Potencial de oxidación (parcialmente modificado de Munter, 2001).

Oxidante	E_0 (V)
Flúor (F_2)	3,03
Radical hidroxilo ($^{\cdot}OH$)	2,80
Oxígeno atómico (O)	2,42
Ozono (O_3)	2,07
Peróxido de hidrógeno (H_2O_2)	1,77
Radical perhidroxilo ($^{\cdot}OOH$)	1,70
Dióxido de cloro (ClO_2)	1,50
Ácido hipocloroso (HClO)	1,49
Cloro (Cl_2)	1,36
Oxígeno (O_2)	1,23

La elevada reactividad de estos radicales, los convierte en especies muy inestables, por lo que tienen que ser generados *in situ* de forma continua. Los métodos de generación de radicales hidroxilo se pueden agrupar de diversas formas, aunque la clasificación más habitual distingue entre los procesos fotoquímicos, que emplean la radiación luminosa, y los no fotoquímicos, en los que los radicales se generan a través de la transformación de especies químicas o mediante la energía aportada por otras fuentes distintas a la luz. En ocasiones, con el fin de conseguir una mayor velocidad de oxidación, o un mayor grado de degradación, dos o más de estos tratamientos se combinan entre sí. La *Tabla 2.4* enumera los distintos procesos de oxidación avanzada existentes, divididos en procesos fotoquímicos y no fotoquímicos.

Tabla 2.4. Clasificación de los procesos de oxidación avanzada

Procesos no fotoquímicos	Procesos fotoquímicos
Ozonización en medio alcalino (O_3/OH^-)	Fotólisis con radiación ultravioleta (UV)
Ozonización con peróxido de hidrógeno (O_3/ H_2O_2)	Ozono y radiación ultravioleta (O_3/UV)
Proceso Fenton (Fe^{2+}/ H_2O_2) Proceso CWPO (catalizador sólido/ H_2O_2)	Peróxido de hidrógeno y radiación ultravioleta (H_2O_2/UV)
Oxidación electroquímica/ electrocatalítica/electro-Fenton	Ozono, peróxido de hidrógeno y radiación ultravioleta (O_3/H_2O_2/UV)
Radiólisis y tratamiento con haces de electrones	Foto-Fenton y relacionadas (Fe^{2+}/H_2O_2/UV) o (catalizador/H_2O_2/UV)
Tratamientos con ultrasonido (O_3/US) (H_2O_2/US) Sono-Fenton (Fe^{2+}-Fe^{3+}/H_2O_2/US)	Fotocatálisis heterogénea (catalizador/UV)

El objetivo final de todos estos tratamientos es la transformación de la materia orgánica en dióxido de carbono y agua. Sin embargo, la mineralización total puede requerir condiciones de operación excesivamente severas, debido a la formación de intermedios refractarios a la oxidación (*Domenech et al., 2001)*, como es el caso de algunos ácidos carboxílicos *viz.* ácido oxálico, acético y fórmico *(Perathoner y Centi, 2005)* y, por lo tanto, puede resultar excesivamente cara. Por ello, llevar a cabo la oxidación parcial de la materia orgánica hasta compuestos biodegradables que no originen problemas de inhibición del crecimiento de biomasa en tratamientos biológicos convencionales, o que permitan la descarga sin originar problemas de ecotoxicidad, se considera una alternativa rentable y eficaz *(Mantzavinos et al., 1999, Santos et al., 2002, Pintar, 2003)*.

Como consecuencia de los elevados costes asociados a las distintas fuentes utilizadas para producir los radicales hidroxilos (O_3, H_2O_2, UV, etc.), los procesos de oxidación avanzada generalmente son aplicables al tratamiento de aguas residuales con concentraciones moderadas de contaminantes orgánicos (DQO=2-20 g/L, como se indicó en la ***Figura 2.3***) *(Matatov-Meytal et al., 1998)*.

De Heredia et al., (2002) realizaron un amplio estudio sobre los costes asociados a los distintos tratamientos de oxidación avanzada cuando éstos fueron empleados para el tratamiento de corrientes acuosas contaminadas con compuestos fenólicos. Los compuestos fenólicos son objeto de múltiples estudios científicos debido a su abundancia en una gran variedad de industrias (papelera, corcho, almazaras, vitivinícola, etc.) y a los problemas de inhibición biológica y de toxicidad que conlleva su presencia en las aguas residuales *(Hamdi, 1992, Yue, 1993)*. Dentro de este grupo de contaminantes se seleccionó el ácido *para*-hidroxibenzoico.

El estudio económico se realizó atendiendo al tiempo de aplicación del tratamiento necesario para reducir 0,1 g/L de contaminante en un 90%. Este cálculo tiene en cuenta los gastos de inversión, la energía eléctrica, los reactivos empleados (especies oxidantes y catalizadores), el agua de refrigeración y los costes de operación y mantenimiento.

La ***Figura 2.5*** muestra la estimación de costes para los distintos procesos de oxidación estudiados, distinguiendo entre procesos no fotoquímicos y fotoquímicos. Puede observarse que los costes se incrementan en gran medida en los procesos en los que interviene la radiación UV. Cabe destacar que la oxidación con peróxido de hidrógeno en presencia de hierro, proceso Fenton, resulta ser el más económico de todos ellos, con costes considerablemente inferiores a los de los sistemas de ozonización. Por su parte, el proceso de oxidación húmeda catalítica con peróxido de hidrógeno (*Catalytic wet peroxide oxidation, CWPO*), en el que se produce la descomposición de peróxido de hidrógeno sobre la superficie de un catalizador heterogéneo (generalmente un catalizador de hierro inmovilizado sobre un material poroso) no fue contemplado en dicho trabajo, debido, probablemente, a que el estudio de dicha tecnología se encontraba en sus comienzos.

Por otro lado, *Esplugas et al. (2002)*, tras comparar los resultados obtenidos con distintos procesos de oxidación avanzada para la eliminación de fenol, entre los que tampoco se contempló la oxidación húmeda con peróxido de hidrógeno, determinaron que el proceso Fenton era el que presentaba una mayor velocidad de degradación de la materia orgánica: 40 veces superior a la radiación UV y a la oxidación fotocatalítica, y 5 veces mayor que la ozonización.

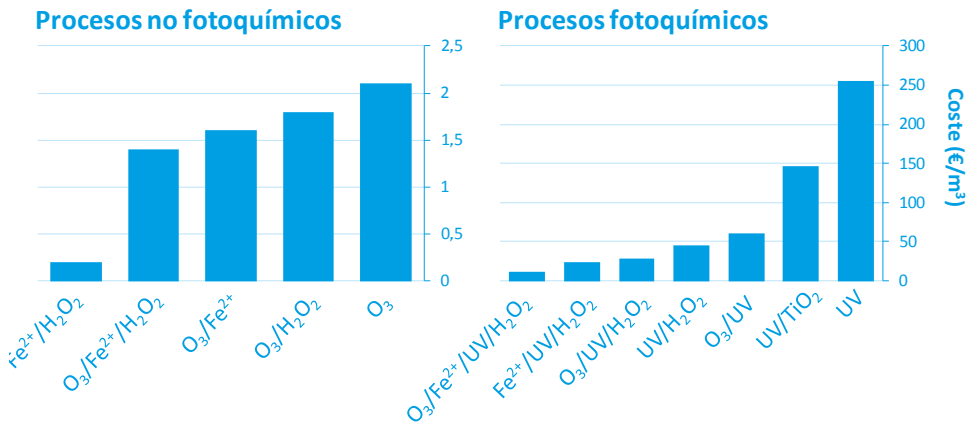

Figura 2.5. Estimación de costes de los procesos de oxidación avanzada. Condiciones de operación: 20 °C, pH=5. (De Heredia et al., 2002)

2.3.1 Proceso Fenton

El proceso Fenton es uno de los procesos de oxidación avanzada más efectivo y económico para la degradación de materia orgánica. Este proceso tiene su origen en el año 1894, cuando H. J. H. Fenton observó que el ácido málico era oxidado en presencia de peróxido de hidrógeno gracias a la acción catalítica de sales de hierro en disolución. Sin embargo, su aplicación en un tratamiento real de oxidación no tuvo lugar hasta finales de la década de los 60 *(Goi y Trapido, 2002)*.

El éxito de este proceso consiste en la generación, en condiciones económicas aceptables, de radicales hidroxilo e hidroperóxido (·OH, ·OOH) por la descomposición

de peróxido de hidrógeno en presencia una sal de hierro divalente disuelta, a pH ácido *(Fenton, 1894)*.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^{-} \qquad [2.1]$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\cdot}OOH + H^{+} \qquad [2.2]$$

La creciente actividad industrial, así como el establecimiento de una legislación ambiental cada vez más severa (apartado 2.1.2), han justificado la intensificación de esta tecnología mediante el endurecimiento de las condiciones de operación *(Zazo et al., 2011, Pliego, 2011)*. El aumento de la temperatura consigue mayores reducciones de materia orgánica en un menor tiempo de reacción y con un menor consumo de reactivos. Así, en la actualidad se emplean presiones en torno a 2-5 atm y temperaturas de hasta 130 °C, condiciones en las que sigue siendo un proceso altamente competitivo, como muestran las numerosas unidades comerciales que aplican esta tecnología en la actualidad *(OHP®)*. La tecnología *OHP®*, creada por la compañía catalana FMC Foret, consiste en la oxidación de la materia orgánica gracias a la utilización de un reactivo basado en peróxido de hidrógeno y sales metálicas como catalizador, en condiciones medias de presión y temperatura (105-130 °C, 1-4 atm). Mediante este proceso es posible eliminar los contaminantes refractarios (compuestos aromáticos, hidrocarburos, colorantes, detergentes, fenoles, naftalenos, etc.), el color y la toxicidad eficazmente, a costes competitivos, al tiempo que se alcanzan elevados rendimientos en la eliminación de DQO (hasta el 99%).

El proceso Fenton (Fe^{2+}/H_2O_2) resulta una solución atractiva gracias a la simplicidad de diseño y la sencillez de operación, debido, por un lado, a la abundancia, bajo

coste y baja de toxicidad del hierro y, por otro, a la facilidad de manejo del peróxido de hidrógeno y su descomposición en productos inocuos para el medio ambiente. No obstante, este proceso también presenta aspectos negativos, como son el elevado precio del peróxido de hidrógeno y la dependencia de la actividad catalítica con el pH del agua a tratar. El sistema Fe^{2+}/H_2O_2 presenta la máxima actividad a un pH en torno a 3 *(Neyens y Baeyens, 2003, Perathoner y Centi, 2005)*, lo que ha de tenerse en cuenta en la selección de los materiales, y obliga a la incorporación de una etapa de ajuste del pH del agua residual antes del tratamiento y la consiguiente neutralización del efluente final. La ***Figura 2.6*** muestra un esquema simplificado de dicho proceso.

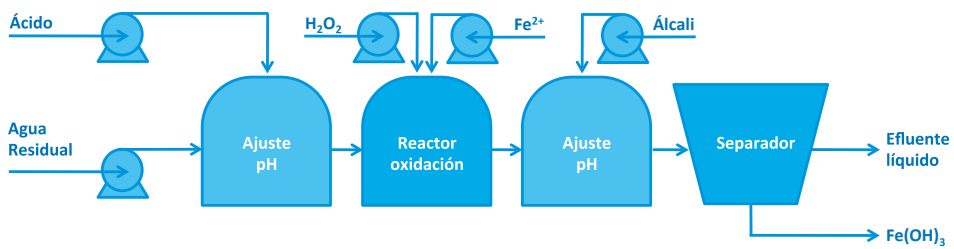

Figura 2.6. Esquema simplificado del proceso Fenton.

Otro inconveniente importante asociado al proceso Fenton deriva de la pérdida continua de catalizador, añadido como sal de Fe^{2+}, en el efluente, que, además, implica la necesidad de separarlo del mismo y gestionar de manera adecuada los lodos de hidróxido de hierro generados en la etapa de neutralización, que pueden arrastrar materia orgánica en suspensión y/o adsorbida.

Una posible solución a este problema consiste en sustituir las sales de hierro por catalizadores sólidos, lo que ha dado lugar al proceso conocido como Oxidación Húmeda Catalítica con Peróxido de Hidrógeno (*Catalytic Wet Peroxide Oxidation, CWPO*).

2.3.2 Oxidación Húmeda Catalítica con Peróxido de Hidrógeno

El empleo de catalizadores heterogéneos, constituidos por una fase activa anclada sobre la superficie de un sólido poroso, permite superar algunas desventajas asociadas al proceso Fenton homogéneo. En primer lugar, el catalizador, al ser sólido, se puede recuperar fácilmente tras la reacción, lo que permite su reutilización, evitando así la pérdida del mismo con la corriente tratada. Por otro lado, al encontrarse la fase activa anclada a la superficie de un soporte sólido, se evita la generación de lodos de hierro en el vertido final. Por último, se espera que estos catalizadores sean activos en un rango de pH más amplio que las sales de hierro.

En la bibliografía existen numerosos estudios sobre el proceso de oxidación húmeda catalítica con peróxido de hidrógeno dedicados al tratamiento de diferentes compuestos orgánicos persistentes mediante el empleo de catalizadores heterogéneos muy diversos. El interés de la comunidad científica en dicha temática ha aumentado en gran medida en los últimos años, como así demuestra el número creciente de artículos desde el año 1996, cuando se publicó el primer trabajo sobre este proceso, hasta la actualidad. La ***Figura 2.7*** muestra esta evolución.

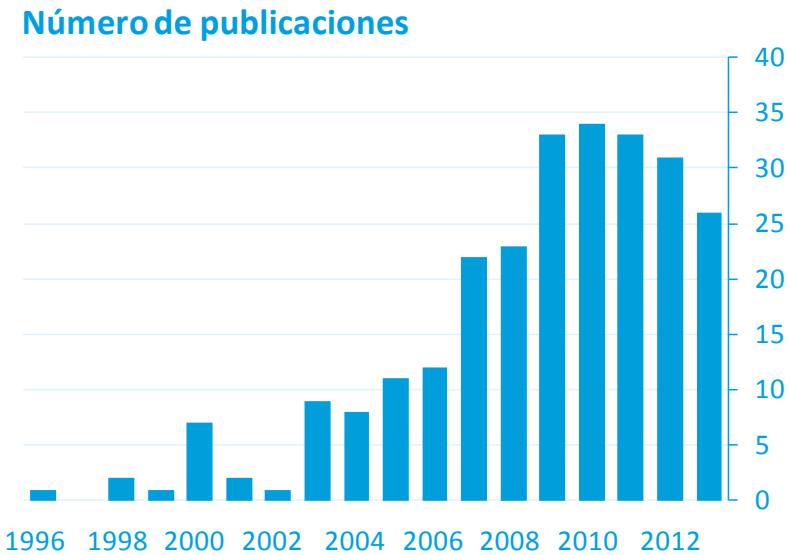

Figura 2.7. Evolución del número de publicaciones sobre el proceso CWPO. Fuente: ISI Web of Knowledge.

No obstante, el número de trabajos dedicados al proceso Fenton continua siendo mucho mayor. Esto es debido, como se comentará posteriormente, a la dificultad de encontrar un catalizador heterogéneo tan activo como las sales de Fe^{2+} empleadas en el proceso homogéneo, a la vez que estable y económico, que haga al proceso CWPO competitivo respecto al proceso Fenton. De ahí, que, a pesar de las claras ventajas que presenta esta tecnología frente al proceso homogéneo, todavía no se haya desarrollado a nivel comercial ningún proceso de oxidación húmeda con peróxido de hidrógeno para el tratamiento de aguas residuales industriales. Un esquema propuesto para este proceso se muestra en la ***Figura 2.8***, en el que se

han eliminado las etapas de neutralización y separación necesarias en el proceso Fenton convencional *(Figura 2.6)*.

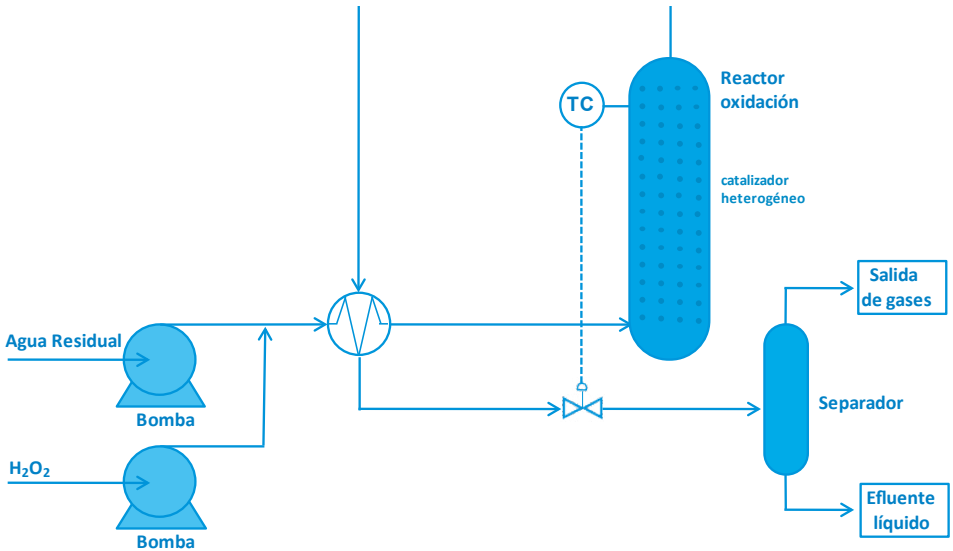

Figura 2.8. Esquema propuesto para una unidad CWPO.

Sobre el total de los trabajos recopilados sobre oxidación húmeda catalítica con peróxido de hidrógeno en la *Figura 2.7*, se presenta una distribución por tipo de contaminantes tratados en dichos estudios, *Figura 2.9*. Como se observa en esta figura, estos procesos han sido aplicados fundamentalmente al tratamiento de contaminantes modelo, siendo el fenol y sus derivados, clorofenoles y nitrofenoles, los que han centrado los mayores esfuerzos, con más de un 50% de las publicaciones y, en segundo lugar, diversos tintes y colorantes orgánicos (*viz.* azul de metileno,

naranja de metilo, rojo ácido, rojo reactivo, negro reactivo, etc.). En general, el fenol es el compuesto modelo escogido en los estudios sobre oxidación avanzada debido a la abundancia de aguas residuales industriales contaminadas por este compuesto tóxico, procedentes de diversas industrias, como la farmacéutica, química, petroquímica, metalúrgica, refino de petróleo, textil y alimentaria y, también, debido a que es un intermedio de la ruta de oxidación de diversos compuestos aromáticos de elevado peso molecular. En los últimos años ha ganado interés el estudio sobre el tratamiento de aguas residuales reales, como las procedentes de la industria cosmética *(Bautista et al., 2010, 2010B)*, petroquímica *(Pariente et al. 2010)*, farmacéutica *(Melero et al., 2009)*, agroquímica *(Pariente et al., 2013)* y de producción de aceite *(de Rosa et al., 2005, Azabou et al., 2010)*.

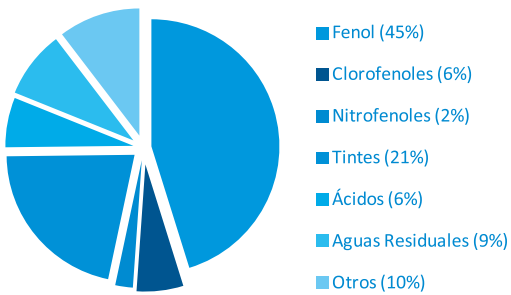

Figura 2.9. Publicaciones científicas sobre el proceso CWPO en función del tipo de efluente tratado. Fuente: ISI Web of Knowledge.

Las condiciones de operación en estos estudios ***(Figura 2.7)*** varían en gran medida de un trabajo a otro, aunque en general éstos se caracterizan por llevarse a cabo

en condiciones relativamente suaves de presión y temperatura. Las temperaturas de reacción ensayadas oscilan entre temperatura ambiente y 160 °C, siendo lo más habitual encontrar trabajos que emplean temperaturas comprendidas entre 50 y 90 °C *(Najjar et al., 2005, Melero et al., 2009, Martínez et al., 2009, Botas et al., 2010, Molina et al., 2010, Rey et al., 2010, Gomes et al., 2010, Catrinescu et al., 2011, Zazo et al., 2012, Centi et al., 2000, Inchaurrondo et al., 2012, Pariente et al., 2013, Munoz et al., 2013, di Luca et al., 2012)*. En la mayoría de los casos, como la temperatura de reacción no supera los 100 °C, se opera a presión atmosférica; en caso contrario se han empleado presiones de hasta 10 bares *(Barrault et al., 2000, Ovejero et al., 2001, Sotelo et al., 2004, Melero et al., 2004, 2006, Calleja et al., 2005)*, con el fin de mantener el medio de reacción en fase líquida. El rango de pH estudiado ha sido entre 2,5 y 8; mucho mayor, por tanto, que el del proceso homogéneo, siendo lo más habitual trabajar a valores de pH del agua residual comprendidos entre 3 y 5,5 *(Barrault et al., 1998, 2000, Centi et al., 2000, Carriazo et al., 2003, 2008, Najjar et al., 2005, Zazo et al., 2006, 2009, 2012, Martínez et al., 2007, 2009, Melero et al., 2007, 2009, Catrinescu et al., 2011, Duarte et al., 2011, Bautista et al., 2011, Rey et al., 2011, Inchaurrondo et al., 2013)*. La concentración de contaminante suele ser igual o inferior a 0,1 g/L, aunque se ha llegado a trabajar con concentraciones del orden de 5 g/L *(Massa et al., 2008, di Luca et al., 2012)* o incluso mayores *(Adam et al., 2010, 2013, Zhao et al., 2011)*; lo que ha provocado el empleo de muy diferentes cargas de catalizador, entre 0,3 y 20 g/L, y porcentaje de fase activa, que varía entre 0,1 y 20% en peso. Las aguas residuales reales tratadas mediante el proceso CWPO presentan, generalmente, una concentración de materia orgánica bastante mayor a la de los efluentes sintéticos, especialmente en el caso de los efluentes procedentes de la producción de aceite *(de Rosa et al., 2005, Azabou et al., 2010)*. Por su parte, la cantidad de peróxido de hidrógeno empleada suele corresponder con la dosis estequiométrica necesaria para la

mineralización de la carga orgánica presente en el agua residual *(Catrinescu et al., 2003, Sotelo et al., 2004, Melero et al., 2004, 2006, Calleja et al., 2005, Zazo et al., 2006, 2009, 2012, Martínez et al., 2007, 2009, Castro et al., 2010, Rey et al., 2010, 2011, Bautista et al., 2010, Botas et al., 2010, di Luca et al., 2012, Munoz et al., 2013, Pariente et al., 2013)*. Sin embargo, no son pocos los trabajos en los que, con el fin de aumentar el grado de oxidación o suavizar las condiciones de operación, en particular, la temperatura, se emplean cantidades de oxidante mucho mayores, entre 5 *(Gomes et al., 2010, Türgay et al., 2011, Ribeiro et al., 2012)* y 10 veces la cantidad estequiométrica *(Guo y Al-Dahhan, 2003, Taran et al., 2013)*, con lo que la eficiencia en el consumo de este reactivo, definido como unidad de DQO convertida por unidad de peróxido de hidrógeno consumida, es baja. A pesar de que este aspecto es determinante para garantizar la viabilidad económica del proceso, son escasos los trabajos que le han dado la relevancia necesaria *(Botas et al., 2010, Martin et al., 2011, Inchaurrondo et al., 2012)*. Por último, los tiempos de reacción abarcan desde minutos hasta días, siendo lo más habitual emplear tiempos de residencia comprendidos entre 2 y 8 horas.

En estos trabajos, los resultados de la oxidación, así como la actividad de los catalizadores empleados, se suelen evaluar mediante el análisis de la evolución del contaminante, en términos de concentración o conversión con el tiempo de reacción, en el caso de emplear reactores *slurry* (reactores tanque discontinuos con el catalizador en suspensión) *(Catrinescu et al., 2003, Melero et al., 2004, 2006, Zazo et al., 2006, 2009, 2012, Calleja et al., 2005, Gomes et al., 2010, Botas et al., 2010, Rey et al., 2010, 2011, Munoz et al., 2013)*, o con el tiempo espacial en el caso de emplear reactores de lecho fijo *(Martínez et al., 2009, Botas et al., 2010, Pariente et al., 2013)*. Cabe destacar el gran número de trabajos que emplean reactores semi-continuos, en los que el efluente a tratar se introduce por cargas y el peróxido de hidrógeno

en continuo, con el fin de aumentar la eficiencia en su consumo *(Barrault et al., 2000, Carriazo et al., 2003, Stolyarova et al., 2007, Caudo et al., 2007, Xiang et al., 2009, Azabou et al., 2010)*. En algunos casos, la medida del compuesto contaminante se complementa con medidas del grado de oxidación (DQO) o de mineralización (COT) alcanzados. Estos parámetros globales (DQO y COT) son especialmente empleados en el caso de aguas residuales reales *(de Rosa et al., 2005, Melero et al, 2009, Bautista et al., 2010, 2010B, Azabou et al., 2010, Pariente et al., 2010, 2013)*.

Como consecuencia de la gran variedad de condiciones de operación empleadas, así como de las diferentes variables respuesta estudiadas, los resultados obtenidos son muy diversos y la comparación de la actividad de los distintos catalizadores ensayados, resulta muy complicada. Sería necesario el empleo de medidas que permitan evaluar de manera directa dicha actividad, tales como velocidades iniciales o el cálculo de parámetros como TON (*turnover number*) o TOF (*turnover frequency*). Desafortunadamente, son muy pocos los estudios en los que se recogen datos sobre dichos parámetros *(Martín et al., 2011)*. Por otro lado, la existencia de fenómenos de lixiviación de la fase activa, por los que el metal soportado se solubiliza en el medio de reacción, provoca que parte de la reacción tenga lugar en dicha fase. La ausencia de experimentos específicos que permitan determinar la contribución homogénea en la reacción de oxidación global, es otro de los factores que dificulta el análisis de la actividad intrínseca de los catalizadores heterogéneos.

2.3.2.1 Catalizadores empleados

Como se ha comentado anteriormente, los catalizadores empleados en este proceso suelen estar constituidos por una fase activa anclada a la superficie de un

sólido poroso. La fase activa cataliza la descomposición de peróxido de hidrógeno en especies radicalarias, mientras que la misión del soporte es retener y distribuir de forma homogénea dicha fase. La utilización de este tipo de catalizadores se encuentra supeditada a que presenten una elevada actividad y estabilidad con el tiempo de uso, junto con una adecuada resistencia física, química y mecánica en las condiciones de operación empleadas *(Matatov-Meital y Sheintuch, 1998)*.

2.3.2.1.1 Fases activas

La ***Figura 2.10*** muestra los trabajos recogidos anteriormente en la ***Figura 2.7***, distribuidos ahora en función de la fase activa empleada. Como se observa, el catalizador más estudiado en el proceso CWPO es el de Fe, dada la elevada actividad que presenta este metal en el proceso Fenton, aunque, en este caso, inmovilizado sobre diferentes soportes porosos, como carbón activado *(Zazo et al., 2006, Quintanilla et al., 2007, Rey et al., 2009)*, alúmina *(Bautista et al., 2010, Inchaurrondo et al., 2012, Munoz et al., 2013)*, sílice *(Melero et al., 2004, 2006, Martínez et al., 2007, Botas et al., 2010)*, zeolitas *(Centi et al., 2000, Pestunova et al., 2002, Valkaj et al., 2011)* o arcillas pilareadas *(Barrault et al., 2000, Catrinescu et al., 2003, Molina et al., 2006)*.

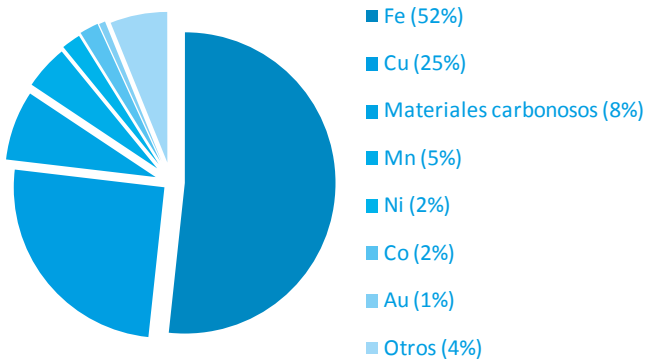

Figura 2.10. Publicaciones científicas sobre el proceso CWPO en función de la fase activa empleada. Fuente: ISI Web of Knowledge.

Además, se han empleado otras fases activas metálicas (M) como Cu, Mn, Ni, Co y Au, con potenciales de oxidación-reducción, que al igual que los del hierro, permiten la descomposición de peróxido de hidrógeno a radicales hidroxilo e hidroperóxido *(Aguado, 2012):*

$$M + H_2O_2 \rightarrow M^+ + {}^{\cdot}OH + OH^- \qquad [2.3]$$

$$M^+ + H_2O_2 \rightarrow M + {}^{\cdot}OOH + H^+ \qquad [2.4]$$

Como ya se ha comentado, el principal problema de los catalizadores empleados en este proceso es, sin duda, la desactivación de los mismos como consecuencia, generalmente, de la lixiviación de la fase activa *(Rokhinay Virkutyte, 2010)*. Por ese motivo, un 8% de los trabajos publicados en este campo ***(Figura 2.10)*** está de-

dicado al empleo de materiales no metálicos y activos en la reacción de descomposición de peróxido de hidrógeno, los materiales carbonosos, siendo el carbón activado el principal material empleado. A pesar de que el número de trabajos es todavía bastante reducido, el interés por estos materiales como catalizadores para procesos de oxidación con peróxido de hidrógeno está creciendo, como así muestra la *Figura 2.11*.

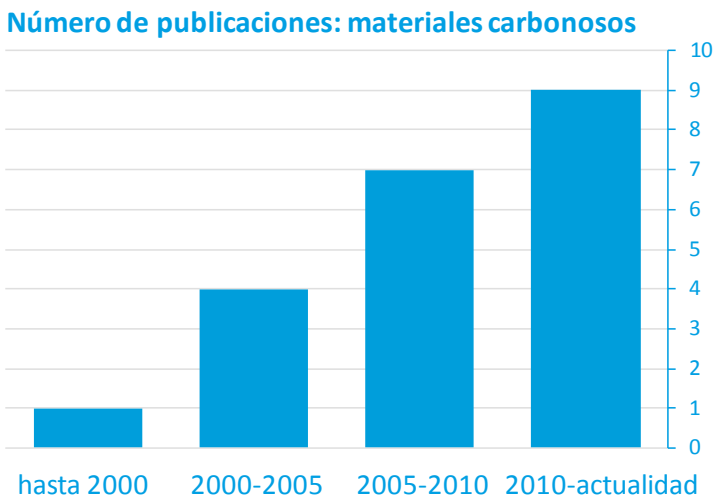

Figura 2.11. Evolución del número de publicaciones sobre el proceso CWPO basadas en materiales carbonosos como catalizadores. Fuente: ISI Web of Knowledge.

2.3.2.1.2 Soportes

Las características de los soportes determinan en gran medida las propiedades finales del catalizador. Éstos se seleccionan atendiendo, principalmente, a dos mo-

tivos: un elevado desarrollo superficial, que permita una dispersión de la fase activa homogénea y elevada, y una elevada estabilidad térmica, mecánica y química, para minimizar los problemas de desactivación. Como consecuencia del importante papel que juega el soporte en el proceso CWPO y, dado que el número de fases activas está limitado a aquellos materiales cuyos potenciales de oxidación-reducción permitan la descomposición de peróxido de hidrógeno, los mayores esfuerzos se han centrado en la búsqueda de soportes adecuados y en la modificación de los mismos, con el fin de optimizar sus características (desarrollo superficial, estabilidad térmica, mecánica y química), para maximizar la actividad de la fase activa y minimizar su lixiviación.

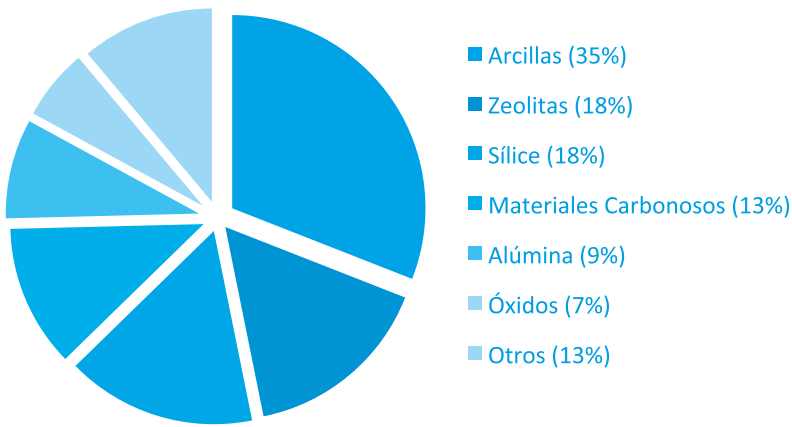

Figura 2.12. Publicaciones científicas sobre el proceso CWPO en función del soporte empleado. Fuente: ISI Web of Knowledge.

La *Figura 2.12* muestra la distribución de los principales materiales empleados como soportes catalíticos en procesos de oxidación húmeda con peróxido de hidrógeno. Éstos son muy variados y el número de contribuciones se distribuye de forma homogénea; entre los materiales más estudiados se encuentran las arcillas, las zeolitas, los materiales silíceos, los materiales carbonosos y la alúmina. Además de éstos, algunos autores han empleado otros tipos de soportes catalíticos, como resinas *(Liou et al., 2005, 2010)*, matrices poliméricas *(Castro et al., 2010, 2013) y MOFs (Metal Organic Frameworks) (de Rosa et al., 2005, Caudo et al., 2007, Granato et al., 2012)*.

A continuación se describirán, de forma detallada, los distintos tipos de soporte empleados en el proceso de oxidación húmeda catalítica con peróxido de hidrógeno.

Catalizadores soportados sobre arcillas

Las arcillas representan el soporte más empleado en el proceso CWPO ***(Figura 2.12)***, en particular, las arcillas pilareadas, las cuales se sintetizan por inserción de policationes metálicos voluminosos mediante intercambio iónico de los cationes existentes en el espacio interlaminar de la arcilla natural (Na^{+}, Ca^{2+}), con el consiguiente aumento del espaciado basal *(Gil et al., 2000)*. El posterior tratamiento térmico hace que los policationes se transformen en óxidos metálicos, los cuales mantienen separadas las láminas de silicato y evitan su colapso, consiguiendo sólidos de elevada área superficial, porosidad accesible y un gran número de centros ácidos.

Dentro de las arcillas, la bentonita es el material de partida más común *(Barrault et al., 1998, 2000, Carriazo et al., 2003, 2005, Guélou et al., 2003, Caudo et al., 2006,*

Molina et al., 2006, Galeano et al., 2012, Bankóvic et al., 2012), aunque también se han empleado otro tipo de arcillas como la sepiolita *(Rodríguez et al., 2010)*, la beidellita *(Catrinescu et al., 2003)*, las saponitas *(Ramirez et al., 2007, Herney-Ramirez et al., 2011, Silva et al., 2012)* y las montmorillonitas *(Timofeeva et al., 2005, Azabou et al., 2007, Catrinescu et al., 2011, Khankhasaeva et al., 2013)*.

Las fases activas soportadas sobre arcillas pilareadas se reducen prácticamente al hierro y el cobre, englobando entre ambos metales más del 97% de las publicaciones encontradas. Recientemente, se han publicado algunos trabajos en los que se ha ensayado la incorporación de otras especies metálicas, como Zr *(Molina et al., 2006)* Mn *(Galeano et al., 2011)* o Ce *(Carriazzo et al., 2007)*. La fase activa puede ser introducida en la estructura de la arcilla durante el proceso de pilareamiento, a través del policatión *(Barrault et al., 1998, 2000)*, o bien, posteriormente, mediante una etapa de impregnación *(Catrinescu et al., 2003)*.

El empleo de las arcillas pilareadas ha dado lugar a resultados muy interesantes, ya que se trata de catalizadores con elevada actividad y alta estabilidad cuando la fase activa se encuentra inmovilizada en el pilar de la arcilla. Así, son numerosos los trabajos que presentan catalizadores, tanto de hierro *(Guo y Al-Dahhan, 2003, Guélou et al., 2003, Catrinescu et al., 2003, 2011, Carriazo et al., 2005, 2008, Caudo et al., 2007, Ramirez et al., 2007, Khankhasaeva et al., 2008, Najjar et al., 2008, Sanabria et al., 2008, 2009, 2010, Bankovic et al., 2009, 2012, Martínez et al., 2009, Molina et al., 2010, Herney-Ramírez et al., 2011, Galeano et al., 2012)* como de cobre *(Kim et al., 2003, Kim y Lee, 2004, Caudo et al., 2007, Achma et al., 2008, 2012)* resistentes a la lixiviación; por lo que pueden ser recuperados y utilizados de nuevo en otro ciclo catalítico. A modo de ejemplo, *Catrinescu et al. (2011)*, empleando un catalizador de Fe soportado

sobre arcilla pilareada, consiguieron la eliminación completa de 4-clorofenol y una mineralización en torno al 60% en tan sólo 2 h de reacción, trabajando a 50 °C y pH=3,5, con una lixiviación de hierro poco significativa (<1 mg/L). El único problema asociado al uso de este catalizador es el elevado consumo de especie oxidante, el cual suele ser empleado en exceso *(Aguado, 2012)*.

Con el fin de mejorar las propiedades mecánicas de estos catalizadores y poderlos adaptar a un lecho fijo para trabajar en continuo, se ha ensayado también su configuración en forma de extruidos *(Guo y Al-Dahhan, 2003, Sanabria et al., 2010)*. Antes de evaluarlos en este tipo de reactores, los catalizadores preparados se ensayaron en reactores tipo *slurry*, en la reacción de oxidación de fenol. En estos trabajos se determinó que la actividad exhibida disminuye sensiblemente respecto al catalizador en polvo, debido a la existencia de limitaciones difusionales *(Sanabria et al., 2010)*. No obstante, los resultados son prometedores; el catalizador Fe/arcilla pilareada, en forma de extruidos, sintetizado por *Guo y Al-Dahhan (2003)*, mostró una elevada estabilidad durante varios ciclos de reacción, manteniendo una adecuada actividad (completa eliminación de fenol a 90 °C y pH=4 a las 4 h de reacción).

Catalizadores soportados sobre zeolitas

Se han empleado numerosos tipos de zeolitas como soporte catalítico en los procesos CWPO, constituyendo el segundo soporte más utilizado ***(Figura 2.12)***. Entre ellas, cabe destacar la zeolita ZSM-5 como soporte empleando hierro, principalmente, como fase activa *(Fajerwerg et al., 1997, 2000, Centi et al., 2000, Ovejero et al., 2001, Phu et al., 2001, Kuznetsova et al., 2004, Najjar et al., 2005, Stolyarova et al.,*

2007, Lázár et al., 2009, Gonzalez-Olmos et al., 2009, Dükkanci et al., 2010, Bolova et al., 2011, Prihodko et al., 2011) y, en menor medida, con cobre *(Pestunova et al., 2002, Perathoner y Centi, 2005, Valkaj et al., 2007, 2011)*. Otras zeolitas empleadas han sido: zeolita USY *(Ovejero et al., 2001, Rodríguez et al., 2010)* zeolita Y *(Larachi et al., 1998, Ovejero et al., 2001, Neamţu et al., 2004, 2004B, Aravindhan et al., 2006, Kondru et al., 2009, Zrncevic y Gomzi, 2005, Fathima et al., 2008, Prihodko et al., 2011)*, zeolita BEA *(Najjar et al., 2005)*, zeolita MFI *(Melero et al., 2004, Calleja et al., 2005)*, zeolita 13X *(Granato et al., 2008, Valkaj et al., 2011, 2011B)*, zeolita L nanocristal *(Adam et al., 2013)* y zeolita tipo clinoptilolita *(Bayat et al., 2012)*.

Los catalizadores soportados sobre zeolitas presentan, en general, una actividad moderada ya que, como consecuencia de su estructura microporosa, presentan problemas difusionales *(Aguado, 2012)*. Además muestran serios problemas de estabilidad, pudiéndose alcanzar importantes pérdidas de metal, *i.e.* 95% para el caso de Fe en la oxidación de fenol (100 °C, 10 atm, Fe/ZSM-5) *(Ovejero et al., 2001)* y del 60% de Cu (80 °C, 1 atm, Cu/13X) *(Valkaj et al., 2011)*. Resulta, por tanto, especialmente importante en el caso de estos materiales, optimizar el método de síntesis de los catalizadores.

Catalizadores soportados sobre materiales silíceos

No son muchos los trabajos que emplean sílice amorfa como soporte catalítico en procesos CWPO *(Cuzzola et al., 2002, He et al., 2003, Huang y Huang, 2008, Rodríguez et al., 2010, Botas et al., 2010, Adam et al., 2010, Satishkumar et al., 2013, Granato et al., 2009)*. Además, los resultados obtenidos con estos catalizadores no son muy prometedores, debido principalmente a su baja estabilidad *(Huang y Huang, 2008,*

Granato et al., 2009, Satishkumar et al., 2013). De este modo, la tendencia en este campo se ha desviado progresivamente hacia la preparación de materiales silíceos mesoestructurados, como el SBA-15, con propiedades más interesantes para la reacción estudiada, los cuales mostraron una mayor actividad, estabilidad y eficiencia que aquellos soportados sobre sílice amorfa *(Calleja et al., 2005)*.

La elevada actividad exhibida por los materiales silíceos mesoestructurados se atribuye, por un lado, a la ausencia de problemas difusionales y, por otro, a la mayor incorporación de fase activa metálica junto a una mejor dispersión superficial que en el caso de otros soportes *(Aguado, 2012)*.

Los soportes catalíticos silíceos mesoestructurados más empleados en la oxidación húmeda con peróxido de hidrógeno son el MCM-41 *(Parvulescu y Su, 2001, Crowther y Larachi, 2003, Gokulakrishnan et al., 2008)* y el SBA-15 *(Calleja et al., 2005, Melero et al., 2006, 2007, 2009, Martínez et al., 2007, 2007B, 2008, Xiang et al., 2009, Pariente et al., 2010, 2013, Botas et al., 2010, Mayani et al., 2012, Zhong et al., 2012, Subbaramaiah et al., 2013, 2013B)*, utilizando principalmente Fe y Cu como fases activas, y observándose resultados similares en cuanto actividad catalítica, independientemente del soporte empleado. Otras fases activas ancladas a soportes silíceos mesoestructurados han sido Mn *(Han et al., 2007, Chaliha y Bhattacharyya, 2008)*, V *(Wu et al., 2009)*, Ni *(Chaliha et al., 2008B)*, Co *(Chaliha et al., 2008B)* y Ce *(Subbaramaiah et al., 2013C)*.

Cabe destacar el catalizador de nanopartículas de óxido de hierro soportadas sobre el tamiz molecular SBA-15 (Fe/SBA-15), desarrollado en el Departamento de Ingeniería Química y Ambiental de la Universidad Rey Juan Carlos *(Calleja*

et al., 2005, Martínez et al., 2007, 2007B, 2008, Melero et al., 2006, 2007, 2009), que presenta una excelente actividad, ya que permite alcanzar conversiones de fenol del 99% y de carbono orgánico total del 70% a los 10 min de reacción a pH=5,5, 100 °C y 10 atm, junto con una estabilidad aceptable (<10% Fe lixiviado) en la CWPO de fenol. En estos trabajos se ha llevado a cabo un amplio estudio de las variables de operación del proceso y se ha conseguido configurar el catalizador en forma de extruidos para su empleo en reactores catalíticos de lecho fijo (*Martínez et al., 2007)*. El catalizador extruido se empleó en la oxidación de fenol a escala de laboratorio a 80 °C, obteniéndose reducciones de COT en torno al 65% (caudal de alimentación=1 cm^3/min y masa de catalizador=2,9 g). A pesar de que la lixiviación de hierro fue poco significativa (Fe lixiviado=1,3% en un ensayo de larga duración), la conversión de COT disminuyó progresivamente (X_{COT}=35%, 34 h).

El principal problema asociado a este tipo de materiales es el elevado coste que implica la preparación de los mismos *(Aguado, 2012)*.

Catalizadores soportados sobre materiales carbonosos

La ***Figura 2.13*** muestra la distribución de los diferentes materiales carbonosos empleados en el proceso CWPO. Como se observa, el carbón activado es, con diferencia, el soporte catalítico más empleado debido, por un lado, a sus excelentes propiedades texturales y, por otro, a su abundante disponibilidad y bajo coste. Aunque en menor medida, también hay estudios sobre el empleo de aerogeles *(Ramirez et al., 2007B, Duarte et al., 2009, 2011)*, resinas compuestas *(Dantas et al., 2006, Liu et al., 2013)*, nanofibras *(Lu et al., 2009, Rodríguez et al., 2010)*, nanotubos de carbón

(Rodríguez et al., 2010) y diamante *(Navalon et al., 2010, Martín et al., 2011, 2011B)*. Las fases activas inmovilizadas sobre soportes carbonosos son más variadas que en el caso de otros soportes, *i.e.* Fe, Au, Cu, Mn, Co, Ni y Cr, aunque el hierro sigue siendo, con diferencia, la más recurrente.

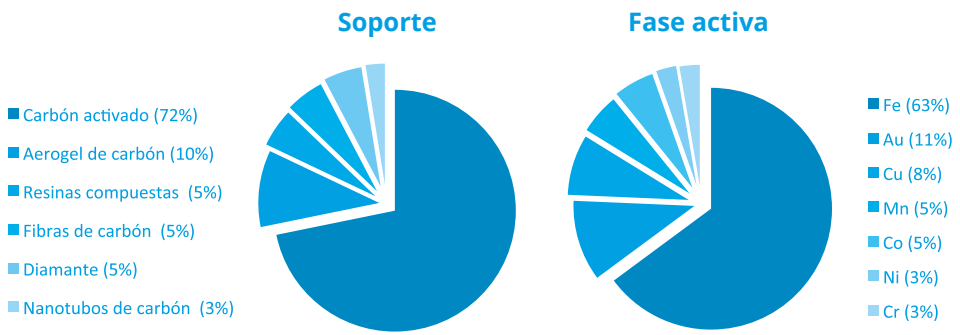

Figura 2.13. Clasificación de las publicaciones científicas sobre el proceso CWPO basados en el uso de materiales carbonosos como soporte. Fuente: ISI Web of Knowledge.

Catalizadores soportados sobre alúmina

La alúmina ha sido empleada principalmente como soporte de Cu y Fe en el proceso CWPO. Estos materiales fueron empleados por primera vez por *Al Hayek et al. (1985)* y *Al Hayek y Doré (1990)* en la oxidación de fenol en condiciones suaves de operación (25-50 °C, P=1 atm), presentando una importante lixiviación de fase activa. Una década después, se volvió al empleo de estos materiales para el tratamien-

to de aguas residuales industriales. En particular, el catalizador Fe/Al_2O_3 fue aplicado con buenos resultados en el tratamiento de aguas residuales de la industria cosmética *(Bautista et al., 2010, 2010B)*. En estos trabajos no se observó lixiviación de fase activa, posiblemente, por la ausencia de ácido oxálico como subproducto de reacción *(Zazo et al., 2006)*.

Cabe destacar el catalizador de hierro-alúmina con propiedades magnéticas desarrollado en la Sección Departamental de Ingeniería Química de la Universidad Autónoma de Madrid, que ha sido empleado para la oxidación de distintos clorofenoles *(Munoz et al., 2013)*. Este catalizador, además de exhibir una adecuada actividad ($X_{contaminante}$=100%, X_{COT}=75%, 4 h) y estabilidad (lixiviación<5%, 100 h), presenta la ventaja de poder ser separado y recuperado fácilmente mediante la aplicación de un imán.

En los últimos años se han publicado también varios trabajos basados en cobre soportado sobre alúmina para la oxidación de diversos colorantes *(Bradu et al., 2010, Zhang et al., 2011)*, clorofenoles *(Li et al., 2011)* y fenol *(Inchaurrondo et al., 2012, 2012B, 2013)*. En este sentido, destacan los importantes problemas de estabilidad asociados a su uso.

Catalizadores soportados sobre otros óxidos metálicos

El empleo de óxidos de hierro como catalizadores representó la primera aproximación a la catálisis heterogénea en la oxidación húmeda con peróxido de hidrógeno. No obstante, aunque el catalizador se adiciona al medio de reacción en estado sólido, la reacción sólo tiene lugar cuando existen iones metálicos en disolución,

actuando el sólido, únicamente, como una fuente continua de catalizador disuelto, con lo que no se solventan los problemas asociados al proceso homogéneo.

Se ha ensayado también la aplicación de otros óxidos metálicos en el proceso CWPO. Así, *Ovejero et al. (2001)* y *Sotelo et al. (2004)* utilizaron distintas perovskitas ($CaTiO_3$) de cobre en la oxidación de fenol, obteniendo conversiones de COT del 94% en 2 h de reacción (a 100 °C y 10 atm). Estos catalizadores pierden actividad como consecuencia de la adsorción de productos carbonosos sobre su superficie y de una importante lixiviación de la fase activa (20%). Uno de los óxidos metálicos más empleados como soporte es CeO_2. Sobre él se han inmovilizado distintas fases activas, como Fe *(Massa et al., 2008, Martins et al., 2010, Yuan et al., 2011)*, Cu *(Massa et al., 2011, Chang et al., 2011)*, Mn *(Lopes et al., 2012)* y W *(Massa et al., 2008)*. El efecto promotor del CeO_2 queda patente en el trabajo de *Massa et al. (2008)*, donde se emplearon sistemas Fe_2O_3/CeO_2 y WO_3/CeO_2 en la oxidación de fenol. En menor medida, TiO_2 también ha sido empleado como soporte catalítico, bien en sistemas mixtos, combinado con CeO_2 *(Zhao et al., 2011, Lopes et al., 2012)*, o por sí solo *(Han et al., 2008)*, al igual que ZnO *(Srikhaow y Smith, 2013)* y ZrO *(Baldrian et al., 2008)*.

2.3.2.1.3 Desactivación de catalizadores

Como se ha evidenciado a lo largo de este capítulo, el principal reto de la oxidación húmeda con peróxido de hidrógeno es la búsqueda de catalizadores activos, eficientes en el consumo de especie oxidante y, fundamentalmente, estables. De ahí, que un numeroso volumen de trabajos esté dedicado a la búsqueda de estrategias para evitar o minimizar la desactivación de los mismos. La principal causa de desactivación de los catalizadores empleados en este proceso es la lixiviación

de la fase activa *(Rokhinay Virkutyte, 2010)* y, en menor medida, la deposición de materia orgánica sobre su superficie. Los fenómenos de lixiviación tienen lugar por diferentes motivos, tales como un débil anclaje de la fase activa al soporte o la elección de condiciones de reacción desfavorables. Con respecto al anclaje de la fase activa, los principales factores que determinan su resistencia a la lixiviación son el tipo de soporte, el tipo precursor de la fase activa, el método de preparación seleccionado, las condiciones de síntesis de los catalizadores y la cantidad de fase activa inmovilizada.

Tipo de soporte

El tipo de soporte seleccionado para la inmovilización de una fase activa determinada puede condicionar la resistencia a la lixiviación de la misma. De forma general, los materiales mesoporosos presentan una menor tendencia a la lixiviación que los zeolíticos *(Aguado, 2012)*, aunque en la bibliografía no existe un criterio claro sobre el tipo de soporte que ofrece una mayor resistencia a este fenómeno.

Calleja et al. (2005) encontraron que la cristalización de la estructura amorfa Fe_2O_3-SiO_2 para dar lugar a una plantilla zeolítica, Fe_2O_3-silicalita, conlleva un importante aumento en la estabilidad de las especies metálicas (7 *vs.* 1 mg/L Fe detectado en el efluente de reacción de la oxidación de fenol a los 90 min, respectivamente). Por su parte, *Rey et al. (2009)*, trabajando con catalizadores de hierro soportado sobre diferentes carbones activados comerciales, todos ellos preparados mediante el método de impregnación húmeda incipiente, determinó que la resistencia a la lixiviación de la especie metálica variaba en gran medida en función del soporte empleado, aunque en general fue alta.

Tipo de precursor

Rey et al. (2009) estudiaron el efecto del precursor de hierro ($Fe(NO)_3$ y $Fe(CO)_5$) en la preparación de catalizadores Fe/carbón activado, concluyendo, tras un análisis de estabilidad en el que pusieron en contacto los catalizadores preparados con una disolución de ácido oxálico (25 mg/L), que el empleo de $Fe(NO)_3$ da lugar a la formación de catalizadores con mayor resistencia a la lixiviación (porcentaje de Fe lixiviado ente el 20 y el 35%) que los de $Fe(CO)_5$ (entre el 35 y el 60%), gracias a un anclaje más fuerte de la fase activa al soporte en el primer caso.

Método de preparación

El método de preparación de los catalizadores condiciona a su vez la manera en la que la fase activa se inmoviliza sobre el soporte. Varios autores han determinado que el modo de introducir la fase activa en las arcillas afecta en gran medida a la lixiviación de dichos metales *(Abdellaoui et al., 1999, Timofeeva et al., 2005). Timofeeva et al. (2005)* encontraron que la arcilla preparada por intercambio iónico a partir de la mezcla de $AlCl_3$-$FeCl_3$, e hidrólisis de la misma (Na_2CO_3), resultó ser mucho más estable que la preparada únicamente a partir del policatión $FeCl_3$ (0,01 *vs.* 19% Fe lixiviado, respectivamente). El método de síntesis también es determinante cuando se emplean otros soportes, como los materiales silíceos tipo SBA-15 *(Calleja et al., 2005, Xiang et al., 2009, Botas et al., 2010)* o las zeolitas *(Valkaj et al., 2007, Bolova et al., 2011, Stolyarova et al., 2007)*. La incorporación de la fase activa durante la propia síntesis del material SBA-15 (co-condensación) es más ventajosa que la posterior etapa de impregnación, ya que conduce a una mayor estabilidad catalítica *(Xiang et al., 2009, Botas et*

al., 2010). Así, *Botas et al. (2010)* determinaron en un ensayo en continuo de oxidación de fenol con peróxido de hidrógeno, que la lixiviación de hierro por parte del material silíceo preparado por síntesis directa fue mucho menor que la correspondiente al material preparado mediante una etapa de impregnación (14 *vs.* 123 mg/L de Fe lixiviado). Esto mismo fue comprobado para el caso de los materiales zeolíticos. *Bolova et al. (2011)* y *Stolyarova et al. (2007)* demostraron que la resistencia a la lixiviación de la fase activa aumenta cuando ésta pertenece a la propia estructura zeolítica; exhibiendo, además, una mayor actividad catalítica *(Phu et al., 2001)*. Por su parte, *Valkaj et al. (2007)* determinaron que la zeolita Cu/ZSM-5 obtenida mediante síntesis directa hidrotermal resultó ser más activa y estable en la oxidación de fenol que la obtenida mediante una etapa de intercambio iónico.

Por su parte, *Zazo et al. (2012),* sintetizaron un catalizador Fe/CA a partir de la activación de lignina con $FeCl_3$, mucho más estable que el correspondiente preparado por impregnación húmeda incipiente, cuando ambos se pusieron en contacto con una disolución de 100 mg/L de ácido oxálico (Fe lixiviado=2 y 100% a las 4 h, respectivamente).

Condiciones de síntesis de los catalizadores

Algunas de las condiciones seleccionadas durante el método de preparación de los catalizadores, como la temperatura, el pH, el tiempo de síntesis, la temperatura de calcinación o la incorporación de etapas de lavado, una vez sintetizado el catalizador, también pueden afectar a la resistencia del mismo frente a la lixiviación de fase activa.

Calleja et al. (2005) determinaron que el valor de pH empleado durante la etapa de envejecimiento del material silíceo SBA-15 es determinante. Así, la selección de un pH muy bajo (<1) conduce a la formación de un sólido con baja resistencia a la lixiviación (el 75% del hierro incorporado al catalizador se lixivia a los 90 min de reacción en la oxidación de fenol), mientras que cuando se trabaja a valores de pH mayores (3,5 y 7), se favorece la formación de óxidos de hierro cristalino (principalmente hematita), lo que permite aumentar en gran medida la resistencia a la lixiviación de fase activa, obteniendo valores de hierro en disolución muy inferiores (8 y 5% Fe lixiviado para pH=3,5 y 7, respectivamente).

Zazo et al. (2009) encontraron que un aumento en la temperatura de calcinación (de 150 a 300 °C) del catalizador Fe/CA, preparado por el método de impregnación húmeda incipiente, aunque mejora las propiedades catalíticas del material gracias a una redistribución de los grupos superficiales oxigenados, no afecta a la resistencia a la lixiviación del hierro, siendo ésta aceptable en todos los casos (<0,5 mg/L). Sin embargo, trabajar a temperaturas de calcinación superiores (hasta 900 °C) parece tener un efecto relevante; así, *di Luca et al. (2012)* también obtuvieron que aumentar la temperatura de calcinación del catalizador Fe/Al_2O_3 permite reducir en gran medida la lixiviación de hierro (del 60 al 7% Fe lixiviado para temperaturas de calcinación de 400 a 900 °C).

Por otro lado, *Al Hayek et al. (1985),* con el fin de reducir la lixiviación de hierro en un catalizador soportado sobre alúmina, lavaron el catalizador antes de introducirlo en reacción (oxidación de fenol). Este tratamiento consiguió reducir la lixiviación de fase activa durante la reacción de oxidación, sin embargo, su actividad también se vio disminuida debido al menor contenido en hierro del catalizador.

Cantidad de catalizador y fase activa inmovilizada

Finalmente, el empleo de altas cargas de catalizador o concentración de especie activa puede promover la lixiviación de la misma. Así, *Ramírez et al. (2007B)*, determinaron que la cantidad de hierro lixiviado aumenta a medida que aumenta la concentración de catalizador (Fe/aerogel de carbón) en el rango 0,15 – 0,3 g/L. Por su parte, *Najjar et al., (2005)* encontraron concentraciones crecientes de hierro disuelto en los efluentes de reacción obtenidos en la oxidación de ácido *p*-cumárico a medida que aumentaba el porcentaje de fase activa soportada sobre el catalizador en el intervalo 3-10% en peso en arcillas pilareadas y zeolitas.

Como ya se comentó al comienzo de este apartado, no sólo la fortaleza del anclaje de la fase activa al soporte influye en la lixiviación de ésta, si no que hay que tener en cuenta además las condiciones de operación a las que se lleva a cabo la oxidación.

Así, las condiciones extremas de reacción, en particular, valores de pH ácidos *(Rey et al., 2000, Najjar et al., 2005, Calleja et al., 2005, Ramirez et al., 2007)* y las altas temperaturas (80-100 °C) *(Sotelo et al., 2004, Bautista et al., 2011)*, favorecen, generalmente, la lixiviación de las especies activas del catalizador. Por este motivo, siempre que sea posible se prefiere el empleo de valores de pH próximos a la neutralidad y temperaturas suaves de operación.

Por otro lado, las altas cargas de especie contaminante también promueven la lixiviación de especie metálica *(Bautista et al., 2011, di Luca et al., 2012)*. Este último caso está asociado a la formación de elevadas concentraciones de intermedios o produc-

tos finales de oxidación, como ácido oxálico, compuesto habitualmente encontrado en la oxidación húmeda con peróxido de hidrógeno de compuestos orgánicos de mayor peso molecular, el cual forma un complejo con el hierro (oxalato de hierro), provocando su lixiviación al medio de reacción *(Zazo et al., 2006, Huang y Huang., 2008, Rey et al., 2009, Bautista et al., 2011, di Luca et al., 2012)*. Este aspecto representa una importante limitación en estos procesos, ya que es difícil inhibir la formación de dicho ácido. Por lo tanto, la aplicación de este proceso, con los catalizadores existentes en la actualidad está restringida al tratamiento de efluentes con una carga de materia orgánica relativamente baja o cuya oxidación no conduzca a la formación de especies intermedias que formen complejos con la fase activa, como así ocurre con el ácido oxálico.

También puede ocurrir, aunque es menos frecuente, la desactivación por deposición de subproductos de oxidación sobre los centros activos del catalizador o sobre la superficie del soporte, taponando los poros del mismo e impidiendo el acceso de reactivos a dichos centros activos. Este tipo de desactivación, a diferencia de la lixiviación, es reversible. Este fenómeno se ha observado, en particular, en los catalizadores de oro soportados, como consecuencia de la adsorción de ácidos carboxílicos sobre las nanopartículas de oro *(Nijhuis et al., 2005, Abad et al., 2008; Martin et al., 2011, 2011B)*. La actividad catalítica puede ser recuperada mediante el lavado del catalizador en medio básico (NaOH) en condiciones ambientales *(Abad et al., 2008, Martin et al., 2011)*. La desactivación por adsorción de productos carbonosos sobre la superficie porosa del soporte se ha detectado en distintos tipos de catalizadores, como hierro soportado sobre arcillas pilareadas *(Catrinescu et al., 2003)*, hierro y cobre soportado sobre alúmina *(Bautista et al., 2010, Zhang et al., 2011)*, hierro soportado sobre carbón activado *(Zazo et al., 2006)* y aerogeles de car-

bón *(Ramirez et al., 2007B)* y cobre sobre perovskitas *(Ovejero et al., 2001, Sotelo et al., 2004)*. En todos ellos la actividad catalítica inicial decrece con el número de usos, pero se puede recuperar mediante una etapa intermedia de calcinación *(Catrinescu et al., 2003, Ramirez et al., 2007B, Zhang et al., 2011)*.

Desafortunadamente y, a pesar de los esfuerzos realizados hasta el momento, son muy pocos los catalizadores heterogéneos, constituidos por la inmovilización de una fase activa sobre un soporte, que sean activos, suficientemente estables, y cuya síntesis no resulte excesivamente cara. Una alternativa razonable sería emplear materiales capaces de catalizar la descomposición de peróxido de hidrógeno a especies radicalarias, sin necesidad de incorporar una fase activa metálica, susceptible de lixiviarse durante la reacción. Así, los materiales carbonosos surgen como catalizadores prometedores en este tipo de procesos. Además, estos materiales presentan importantes ventajas frente a otros sistemas catalíticos, como son su abundancia, origen renovable y bajo coste.

2.3.2.2 Catalizadores basados en Materiales Carbonosos

Como se ha comentado anteriormente, los materiales carbonosos, entre los que destaca por su frecuencia de uso, el carbón activado, han sido empleados en procesos de oxidación húmeda con peróxido de hidrógeno, tanto como catalizadores como soportes catalíticos de distintas fases activas (Fe, Au, Cu, Mn, Co, Ni, Cr). Gracias a sus interesantes propiedades texturales, su química superficial y coste asequible, comparado con otro tipo de materiales, han adquirido recientemente un papel muy importante en este proceso.

El carbón activado se define como un material carbonoso, de estructura porosa altamente desarrollada y con una elevada superficie específica *(Bansal et al., 1988)*. Los átomos de carbono se agrupan en estructuras aromáticas, condensadas y planas que se acoplan de forma irregular, dejando espacios intersticiales entre ellas, que dan origen a la formación de poros. Gracias a ello, son unos excelentes adsorbentes, lo que puede suponer una clara ventaja al concentrar el contaminante en zonas cercanas a los centros activos, donde se producen las especies radicalarias *(Aguado, 2012)*. Los átomos de carbono de los bordes de los planos basales pueden combinarse con otros heteroátomos, generando grupos superficiales, principalmente, oxigenados. Cuando el carbón activado es empleado como soporte catalítico, los grupos superficiales oxigenados actúan como centros de anclaje sobre los que se inmovilizan las distintas fases activas. La ***Figura 2.14*** muestra un esquema de la superficie de un carbón activado, en el que se incluyen los distintos grupos superficiales oxigenados de carácter ácido (representados en color azul) y básico (en color rojo), así como los electrones deslocalizados de los anillos aromáticos del carbón.

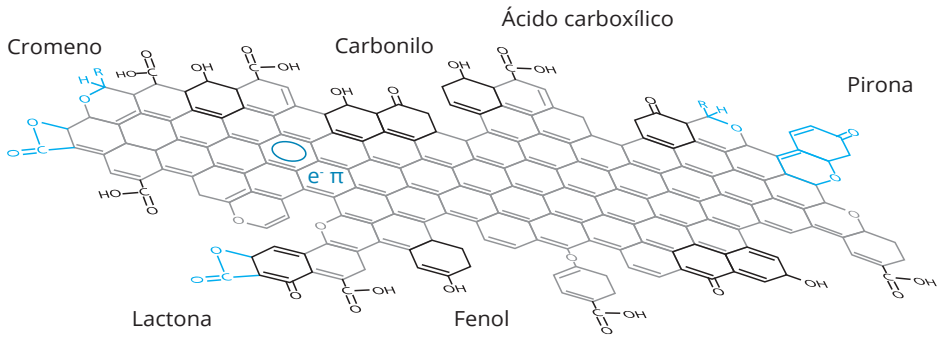

Figura 2.14. Carácter ácido (negro) de algunos GSO y básico (azul) determinado por los electrones π desapareados y algunos GSO de la superficie de un carbón activado.

Los carbones activados presentan propiedades superficiales oxido-reductoras que son las responsables de su actividad catalítica en la reacción de descomposición del peróxido de hidrógeno a radicales hidroxilo e hidroperóxido, esquematizada en la *Figura 2.15*.

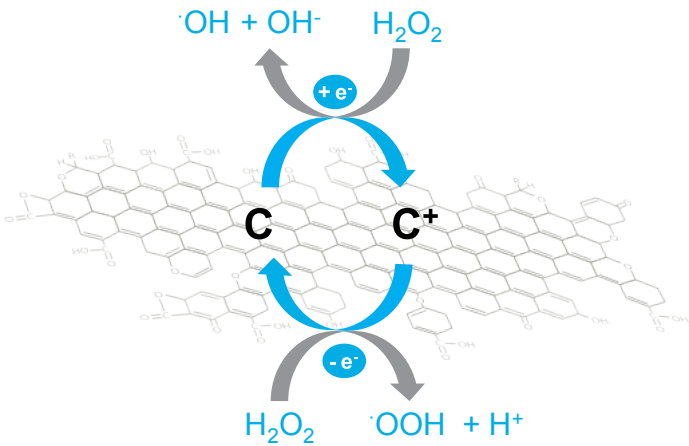

Figura 2.15. Descomposición de peróxido de hidrógeno sobre la superficie de materiales carbonosos mediante un mecanismo de transferencia de electrones. C y C⁺ son los estados reducido y oxidado del carbón activado, respectivamente.

Los centros responsables de la generación de los radicales hidroxilo en la superficie del carbón son los centros de carácter básico, que engloban los grupos básicos de Brønsted-Lowry (grupos oxigenados de carácter básico, principalmente cromenos y pironas) y los centros básicos de Lewis (centros libres de oxígeno, constituidos por los electrones π deslocalizados de los planos basales de los carbones activados) ***(Figura 2.14)*** *(Leon y Leon, 1992)*. Todo apunta a que estos últimos, muy numerosos

debido a la elevada superficie específica que presentan los carbones activados, son los principales centros activos, responsables, por tanto, de la transferencia de electrones por parte del carbón a la molécula de peróxido de hidrógeno, reduciéndose ésta a radicales hidroxilo y dejando el carbón en su forma oxidada (C^+), y a la consiguiente etapa de oxidación de peróxido de hidrógeno a radicales hidroperóxido, por la cual los centros activos de la superficie carbonosa son regenerados (C).

Los factores más determinantes en el proceso de transferencia electrónica y, por tanto, en la actividad catalítica de los sólidos carbonosos para descomponer el peróxido de hidrógeno, son el contenido en cenizas *(Pakula et al., 1998, Rey et al., 2008, Taran et al., 2010, Aguinaco et al., 2011)*, la porosidad *(Lücking et al., 1998, Khalil et al., 2001, Rey et al., 2011)* y la composición química, especialmente la cantidad y naturaleza de los grupos superficiales oxigenados *(Huang et al., 2003, Oliveira et al., 2004, Rey et al., 2008, Santos et al., 2009, Taran et al., 2010)*. Debido a que no es posible aislar cada uno de estos aspectos y estudiar de forma individualizada su influencia en la actividad, y a que, en ocasiones, estos factores presentan efectos contrapuestos en la actividad catalítica, no ha sido posible elucidar, hasta el momento, la importancia relativa de cada uno de ellos, aunque se sabe que el contenido en cenizas, en particular Fe, es especialmente importante.

En las ***Tablas 2.4*** y ***2.5***, se han resumido los trabajos más relevantes publicados sobre el uso de materiales carbonosos en la oxidación húmeda con peróxido de hidrógeno cuando se emplean como soporte catalítico y como catalizador, respectivamente. En estas tablas se ha recogido información sobre la fase activa empleada (cuando procede), el tipo de material carbonoso, el contaminante a tratar, las condiciones de operación empleadas y los resultados más relevantes obtenidos

en dichos trabajos. Dada la relevancia de la estabilidad de los catalizadores en el proceso estudiado, se ha puesto especial interés en recoger los resultados relativos a este aspecto.

Como se deduce de la información recopilada en la ***Tabla 2.4***, la reacción más estudiada es la oxidación húmeda de fenol con catalizadores de hierro soportado sobre carbón activado (Fe/CA). El primer trabajo dedicado a esta temática fue publicado por *Zazo et al. (2006)*, en el que, trabajando con un catalizador Fe/CA preparado por el método de impregnación húmeda incipiente (4% Fe), obtuvieron resultados prometedores, X_{fenol}=100%, X_{COT}=85% en 4 h de reacción con la dosis estequiométrica de peróxido de hidrógeno para la oxidación completa de fenol a 50 °C y pH=3. Sin embargo, la importante contribución de la adsorción en la eliminación de la materia orgánica, que supuso cerca del 50% del COT total eliminado, y la presencia de Fe en disolución (50% del Fe presente en el catalizador, tras 170 h de uso), responsable de que parte de la reacción ocurra en fase homogénea, hace prácticamente imposible conocer la actividad intrínseca del catalizador.

En trabajos posteriores de estos autores, se mostró un catalizador Fe/CA estable, preparado por la activación química de lignina con $FeCl_3$ *(Zazo et al., 2012)*. Mediante este procedimiento de síntesis se consiguió introducir el hierro en la propia matriz carbonosa, aumentando así su estabilidad. Bajo idénticas condiciones de operación que las empleadas en el trabajo anteriormente nombrado (dosis estequiométrica de H_2O_2, 50 °C y pH inicial=3), se obtuvieron rendimientos de oxidación ligeramente inferiores, X_{fenol}=98%, X_{COT}=64% (4 h), lo cual se atribuye principalmente al menor contenido en hierro por parte de este catalizador (1,1 *vs.* 4%). Con el fin de aumentar su actividad, se ensayaron mayores temperaturas de reacción, consiguiendo

una eliminación completa de fenol y una reducción de COT en torno al 70% a 90 °C y 4 h de reacción. En todos los casos el hierro en disolución fue inferior a 0,1 mg/L, lo que demuestra la elevada estabilidad del catalizador.

Cabe destacar también, por la resistencia a la lixiviación de la fase activa, los trabajos de *Lu et al. (2009)* sobre la oxidación de nitrofenol en presencia de un catalizador de Co sobre fibras de carbón activado, de *Kong et al. (2012)*, sobre la oxidación de fenol con un catalizador Mn/carbón mesoporo con estructura hexagonal, y de *Martin et al., (2011)*, también dedicado a la oxidación de fenol, en este caso, en presencia de un catalizador Au/diamante. En estos trabajos, bajo condiciones de operación ambientales o próximas a las ambientales (50 °C en *Martin et al., 2011*; 60 °C en *Kong et al., 2012*), se obtienen conversiones de especie contaminante en torno al 95-100%, en tiempos de reacción comprendidos entre 5 y 7 h.

Resultan particularmente interesantes los resultados obtenidos con el catalizador Au/diamante, ya que permiten alcanzan similares grados de oxidación que los catalizadores anteriormente citados *(Lu et al., 2009, Kong et al., 2012)*, pero empleando cantidades de peróxido de hidrógeno inferiores a la estequiométrica (40% de la cantidad necesaria para la oxidación de fenol a CO_2 y H_2O), lo que es indicativo de una elevada eficiencia en el consumo de especie oxidante *(Martin et al., 2011, 2011B)*. Por tanto, el catalizador Au/diamante abre la puerta al desarrollo de catalizadores basados en nanopartículas de oro inmovilizadas sobre otro tipo de soportes más económicos que el diamante. En este sentido, se ha ensayado el empleo de otros materiales carbonosos, como el carbón activado *(Han et al., 2008, Yang et al., 2013)*. En este caso se obtienen actividades más modestas, $X_{\text{bis-fenol A}}$=89%, a 40 °C y 12 h) *(Yang et al., 2013)* y X_{fenol}=19%, a 70 °C y 2 h *(Han et al., 2008)*, incluso cuando la can-

tidad de peróxido de hidrógeno adicionada es muy superior a la estequiométrica *(Han et al., 2008)*.

Es llamativo el hecho de que, cuando se emplean como soporte catalítico aerogeles de carbón, indistintamente de la fase activa inmovilizada, ***viz.*** Fe, Ni, Co *(Duarte et al., 2009)*, los rendimientos de la oxidación son, en general, perores, por lo que son necesarios tiempos de reacción de más de 24 h para obtener conversiones de contaminante (naranja de metilo) entre el 40 y el 80%. Además, la resistencia a la lixiviación por parte de estos materiales es relativamente baja, lo que conduce a su desactivación con el número de usos. En esta línea, *Ramírez et al., 2007* encontraron que el catalizador Fe/aerogel de carbón presenta una alta actividad en la eliminación de colorantes (X_{COT}=90%, 4 h); sin embargo, la lixiviación de hierro por parte del catalizador fue elevada (≈10%), con lo que la actividad disminuyó considerablemente en usos sucesivos.

A parte de la lixiviación de la fase activa, es de reseñar también la pérdida de actividad sufrida por los materiales carbonosos durante el proceso de oxidación como consecuencia de la adsorción sobre su superficie de determinados subproductos de reacción *(Zazo et al., 2006, Bautista et al., 2010, Li et al., 2010, Dhaouadi y Adhoum, 2010, Martin et al., 2011, Kong et al., 2012, Yang et al., 2013)*.

La *Tabla 2.5* resume los principales trabajos publicados sobre oxidación húmeda con peróxido de hidrógeno con materiales carbonosos como catalizadores en función del tipo de sólido carbonoso empleado. Como se puede apreciar, los mayores esfuerzos se han centrado en el tratamiento de diversos colorantes orgánicos y algunos compuestos fenólicos. En algunos trabajos se aborda la oxidación de de-

terminados compuesto específicos como etanol y ácido fórmico *(Taran et al., 2010)*, herbicidas *(Dhaouadi y Adhoum., 2010)* y metil-terc-butil éter (MTBE) *(Georgi y Kopinke, 2005)*.

La ***Figura 2.15*** muestra la distribución de los trabajos publicados, recogidos en su mayoría en la ***Tabla 2.5*** en función del tipo de material carbonoso empleado. Como puede observarse, los carbones activados son los materiales más empleados, seguidos de los materiales grafíticos y los nanotubos/nanofibras de carbón.

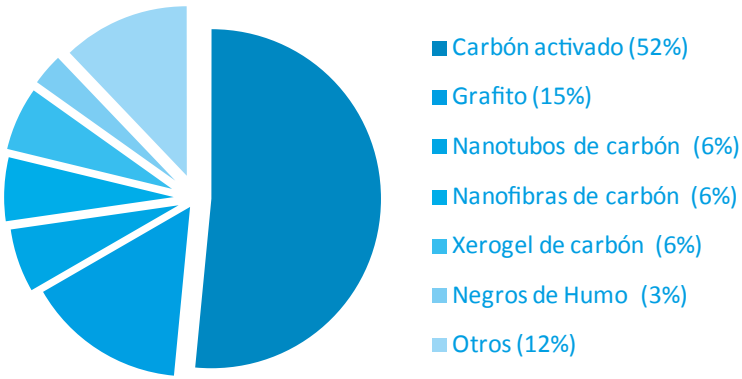

Figura 2.15. Clasificación de las publicaciones científicas sobre el proceso CWPO basadas en el uso de materiales carbonosos como catalizadores. Fuente: ISI Web of Knowledge.

Los carbones activados como catalizadores en procesos CWPO han sido empleados principalmente para la eliminación de diversos colorantes orgánicos *(Oliveira et al., 2004, Santos et al., 2009, Gomes et al., 2010, Duarte et al., 2011, Türgay et al.,*

2011, Gomes et al., 2011, Soria-Sánchez et al., 2012, Gu et al., 2013). Las condiciones de operación empleadas en estos trabajos son variadas, desde 25 hasta 80 °C, lo que conduce a una importante variedad de resultados experimentales, que también se ven modificados en función de la naturaleza del colorante a tratar. No obstante, los grados de oxidación alcanzados en todos ellos son moderados, incluso cuando en numerosas ocasiones se han empleado dosis de peróxido de hidrógeno significativamente superiores a las requeridas para la mineralización de dichos contaminantes *(Oliveira et al., 2004, Santos et al., 2009, Gomes et al., 2010, 2011, Duarte et al., 2011, Soria-Sánchez et al., 2012)*. De este modo, parecen ser habituales, bajas eficiencias en el consumo de peróxido de hidrógeno con los catalizadores de carbón activado debido a que tiene lugar, en gran extensión, la producción de reacciones parásitas de recombinación radicalaria, ecuaciones *2.5-2.7*. Este aspecto es de vital importancia para la viabilidad de los procesos de oxidación húmeda con peróxido de hidrógeno *(Botas et al., 2010, Martín et al., 2011, Inchaurrondo et al., 2012)*, ya que afecta directamente a la economía del proceso.

$$\cdot OH + \cdot OOH \rightarrow O_2 + H_2O \quad [2.5]$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2 \quad [2.6]$$

$$\cdot OOH + \cdot OOH \rightarrow O_2 + H_2O_2 \quad [2.7]$$

Del mismo modo que cuando los carbones activados son empleados como soportes catalíticos, la contribución del fenómeno de adsorción en la eliminación de los contaminantes es muy importante. Por tanto, la evaluación de la actividad catalítica intrínseca de estos materiales sólo sería posible si fueran empleados en procesos

en continuo o en ciclos de reacción consecutivos, de modo que el efecto de la adsorción dejara de ser significativo. En este sentido, son pocos trabajos que se ocupan de este aspecto. Cabe destacar el trabajo de *Gomes et al., 2010,* en el que emplean un carbón activado modificado con ácido sulfúrico, con el fin de aumentar su carácter ácido, para la degradación del colorante ácido Cromotropo 2R con peróxido de hidrógeno. Este catalizador mostró una ligera pérdida de actividad del primer al segundo uso, como consecuencia de la disminución de su capacidad de adsorción, manteniéndose prácticamente constante en usos sucesivos. Otra alternativa estudiada *(Duarte et al., 2011)* ha sido el empleo de carbones activados previamente lavados en una disolución que contiene el colorante a tratar. De este modo, cuando el carbón se pone en contacto de nuevo con el efluente, se encuentra en equilibrio de adsorción, anulándose o minimizándose, por tanto, esta contribución, y permitiendo evaluar su papel como catalizador. En este caso, los tiempos de reacción requeridos para alcanzar grados de conversión aceptables son muy elevados (X_{color}=90%, 24 h) *(Duarte et al., 2011).*

Los carbones activados han sido relativamente poco empleados para el tratamiento de los compuestos modelo típicamente empleados en CWPO, como fenol y sus derivados *(Lüking et al., 1998, Huang et al., 2003, Zazo et al., 2006, Rey et al., 2008, Dehkordi y Ebrahimi, 2009, Ribeiro et al., 2013).* El motivo es que, en estos casos, a pesar de consumirse por completo el peróxido de hidrógeno (cantidad estequiométrica), la eliminación de fenol es debida, principalmente, a su adsorción sobre la superficie carbonosa *(Zazo et al., 2006, Rey et al., 2008, Dehkordi y Ebrahimi, 2009, Ribeiro et al., 2013)*; hecho que se confirmó también para el caso de 2-nitrofenol *(Ribeiro et al., 2013).* Mayores temperaturas de operación (70 °C) y cantidades de peróxido de hidrógeno superiores a la estequiométrica, han sido requeridas para alcanzar grados significa-

tivos de oxidación de este tipo de compuestos (X_{fenol}=100%, 3 h) *(Dehkordi y Ebrahimi, 2009)*. Como consecuencia de emplear cantidades de peróxido de hidrógeno superiores a la estequiométrica, la eficiencia en el consumo de especie oxidante es baja.

Este aspecto, la eficiencia en el consumo de peróxido de hidrógeno, representa un importante inconveniente para la potencial aplicación de los carbones activados como catalizadores en los procesos CWPO. La actividad catalítica de estos materiales depende de poder mantener una alta selectividad hacia la reacción de oxidación del contaminante orgánico e inhibir, en la medida de lo posible, las reacciones parásitas de recombinación radicalaria, ecuaciones *[2.5-2.7]*. Con el fin de mejorar este aspecto y, dado que la química superficial de estos materiales juega un papel importante en dicha reacción, se ha estudiado la posibilidad de introducir grupos superficiales oxigenados (GSO). Atendiendo a los resultados obtenidos, los GSO de carácter ácido disminuyen la actividad de los carbones activados en la descomposición de peróxido de hidrógeno *(Khalil et al., 2001, Huang et al., 2003, Santos et al., 2009, Gomes et al., 2010, Rey et al., 2011)*. Estos grupos son electrón-atrayentes, por lo que disminuyen la densidad electrónica de los planos basales, de modo que la reducción de peróxido de hidrógeno es más progresiva y, por tanto, la producción de radicales. De esta forma se consigue reducir la extensión de reacciones parásitas y aumentar la oxidación de los contaminantes orgánicos *(Huang et al., 2003)*. Por otro lado, los GSO de carácter básico favorecen la reducción de peróxido de hidrógeno a radicales hidroxilo *(Khalil et al., 2001, Oliveira et al., 2004, Rey et al., 2008, 2011)*, liberándolos al medio de reacción y minimizando su recombinación en superficie, de modo que, debido a la mayor presencia de especies oxidantes, el rendimiento global de la oxidación aumenta.

A pesar de todos los estudios llevados a cabo con el fin de mejorar la eficiencia en el consumo de peróxido de hidrógeno, el empleo de carbones activados en la

eliminación de compuestos tipo fenólicos, con un consumo eficiente del oxidante, sigue siendo una cuestión sin resolver. Sería por tanto, interesante profundizar en el estudio de estos materiales con el fin de obtener adecuados grados de oxidación y mineralización, manteniendo un consumo eficiente de peróxido de hidrógeno, de modo que se puedan aprovechar las ventajas asociadas al empleo de este tipo de materiales, como su bajo coste y origen renovable.

En menor medida que los carbones activados, se han empleado materiales grafíticos como catalizadores en procesos CWPO. Estos materiales fueron empleados por primera vez por *Lücking et al. (1998)* en la oxidación de 4-clorofenol, siendo los resultados obtenidos (X_{DQO}=30%, 100 h, a 30 °C y pH=3) poco esperanzadores. Sin embargo, los grafitos porosos o de alta superficie especifica (380 m^2/g, *(Taran et al., 2010)* permiten alcanzar conversiones algo mayores (X_{fenol}=75-86%, 3-100 h) para el tratamiento de fenol *(Pestunova et al., 2003, Taran et al., 2010)* y de colorantes ($X_{colorante}$=55%, 3 h) *(Soria-Sánchez et al., 2012).* No obstante, parte de la eliminación de contaminante es debida a la adsorción *(Soria-Sánchez et al., 2012)* y pierden actividad con el número de usos *(Pestunova et al., 2003).* En los últimos años, otros materiales carbonosos, ***i.e.*** nanotubos, nanofibras, xerogeles, nanodiamantes, han sido estudiados *(Taran et al., 2010, Soria-Sánchez et al., 2012, Ribeiro et al., 2012, 2013)* sin presentar resultados relevantes en las condiciones de operación empleadas ***(Tabla 2.5)***. Cabe destacar el trabajo desarrollado por *Ribeiro et al. (2013)* con nanotubos de carbono, en el que se consiguió reducir el contenido en 2-nitrofenol en un 94% en tan sólo 3 h de reacción. En este sentido, llama la atención que no se hayan empleado otros materiales carbonosos más económicos que los anteriores, como los negros de humo.

Tabla 3.4. Fase activa, tipo de material carbonoso empleado como soporte en el proceso CWPO, contaminante tratado, condiciones de operación empleadas y resultados más relevantes

Fase activa	Soporte	Contaminante	Condiciones operación	Resultados	Estabilidad	*Referencia*
Fe	nanocompuestos de óxido de grafeno reducido	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,01 - 0,3 - 2 g/L T=25 ºC, P=1 atm, pH=5-9	X_{cont}>90% (t=120 min)	$Fe_{lixiviado}$<1,16 mg/L pérdida de actividad<10% en 5 ciclos	*Liu et al., 2013*
Fe	carbón activado	2-nitrofenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,1 - 1,2 g/L T=50 ºC, P=1 atm, pH=3	$X_{cont\ CWPO,\ ads}$=100%, 30% (t=150 min)	$Fe_{lixiviado}$<0,4 mg/L (1,5%)	*Ribeiro et al., 2013*
Fe	carbón activado	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,625 - 0,5 g/L T=50 ºC, P=5 atm	X_{COT}=80% (t=60 min) imp. contribución adsorción	$Fe_{lixiviado}$<0,4 mg/L (1,5%)	*Martínez et al., 2012*
Fe	carbón activado	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,5 - 0,5 g/L T=50-90 ºC, P=1 atm, pH=3	$X_{cont,COT}$=100%, 68% (t=240 min) imp. contribución adsorción	$Fe_{lixiviado}$ despreciable alta estabilidad	*Zazo et al., 2012*
Fe	carbón activado	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 4 - 0,5 g/L T=50 ºC, P=1 atm, pH=3	X_{cont}=90% (t=10 min)	$Fe_{lixiviado}$=1-3 mg/L	*Liu et al., 2012*
Fe	carbón activado	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,02 - 2 - 1,7 g/L T=25 ºC, P=1 atm, pH=7	X_{cont}=90% (t=300 min)	-	*Yang et al., 2012*
Fe	carbón activado	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,2 - 0,5 - 1 g/L T=25 ºC, P=1 atm, pH=3	X_{COT}=90% (t=300 min) (proceso híbrido con fotocatálisis, TiO_2)	$Fe_{lixiviado}$<2 mg/L Estable 4 ciclos	*Rey et al., 2011*
Fe	carbón activado	colorante	$C_{cont\text{-}H2O2}$=0,1 - 6 mM, C_{cat}=0,1 g/L T=30 ºC, P=1 atm, pH=3	$X_{Color,COT}$=90% (t=4 h), 61% (24 h) imp. contribución adsorción	$Fe_{lixiviado}$=1,7%	*Duarte et al., 2011*
Fe, Mn	carbón activado	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,05 - 2,5 - 0,625 g/L T=29 ºC, P=1 atm, pH=4	X_{cont}=100% (t=80 min) (30% debido a adsorción)	$Fe,Mn_{lixiviado}$<0,5-0,25 mg/L desactivación con el uso	*Nguyen et al., 2011*

Fase activa	Soporte	Contaminante	Condiciones operación	Resultados	Estabilidad	*Referencia*
Fe	carbón activado	aguas reales industria cosmética	$C_{COT\text{-}cat}$=1,1 - 5 g/L, H_2O_2 esteq. T=55-85 °C, P=1 atm, pH=3	X_{COT}=15% (t=60 min) (debido a adsorción)	desactivación	*Bautista et al., 2010*
Fe	carbón mesoporoso ordenado	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,25 - 0,6 - 1,8 g/L T=80 °C, P=1 atm, pH=3	$X_{cont,COT}$=93%, 61% (180 min)	desactivación	*Li et al., 2010*
Fe	carbón activado nanotubos de carbón nanofibras de carbón	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,07 - 2 - 0,35 g/L T=30 °C, P=1 atm, pH=3	X_{cont}=80% (60% adsorción) X_{cont}=65% (60% adsorción) X_{cont}=72% (70% adsorción)	$Fe_{lixiviado}$=58% $Fe_{lixiviado}$=29% $Fe_{lixiviado}$=27%	*Rodríguez et al., 2010*
Fe	carbón activado	herbicida	$C_{cont\text{-}cat}$=0,02-0,25 g/L, C_{H2O2}=1-5·esteq T=25-70 °C, P=1 atm	X_{DQO}=85% (180 min) contribución adsorción	actividad disminuye ligeramente con los usos	*Dhaouadi et al., 2010*
Fe	carbón activado	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,5 - 0,5 g/L T=50 °C, P=1 atm, pH=3	$X_{cont,COT}$=100%, 80% (t=120 min) imp. contribución adsorción (40%)	$Fe_{lixiviado}$=0,5 mg/L estabilidad aceptable	*Zazo et al., 2009*
Fe	carbón activado	2,4-Clorofenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,4 - 2 - 3,4 g/L T=25 °C, P=1 atm, pH=3	X_{cont}= 80% (t=180 min)	-	*Yang et al., 2009*
Fe	aerogel de carbón	colorante	$C_{cont\text{-}H2O2}$=0,1 - 6 mM, C_{cat}=0,2 g/L T=30 °C, P=1 atm, pH=3	X_{cont}=80% (t=24 h)	$Fe_{lixiviado}$=0,02 mg/L (0,6%) Pierde actividad con los usos	*Duarte et al., 2009*
Fe	carbón activado aerogel de carbón	colorante	$C_{cont\text{-}H2O2}$=0,1 - 6 mM, C_{cat}=0,2 g/L T=30 °C, P=1 atm, pH=3	X_{COT}= 80% (t=240 min), X_{ads}=50% X_{COT}= 90% (t=240 min), X_{ads}=35%	$Fe_{lixiviado}$=1,2 mg/L (<10%) $Fe_{lixiviado}$=1,5 mg/L (<10%), desactivación	*Ramírez et al., 2007B*

Fase activa	Soporte	Contaminante	Condiciones operación	Resultados	Estabilidad	*Referencia*
Fe	carbón activado	fenol	$C_{cont,cat,H2O2}$=1 - 2,5 - 5 g/L T=23-100 ºC, P=1-8 atm, pH=3,5	$X_{cont,COT}$=95%, 20% (t=40 g_{cat}·h/g_{fenol}, 60 ºC) (combinación CWPO-CWAO)	$Fe_{lixiviado}$<2%	*Quintanilla et al., 2007*
Fe	carbón activado	fenol	$C_{cont-cat-H2O2}$=0,1 - 0,5 - 0,5 g/L T=50 ºC, P=1 atm, pH=3	$X_{cont,COT}$=100%, 85% (t=240 min) imp. contribución adsorción (50%)	$Fe_{lixiviado}$ (50%, 170 h) pérdida de actividad	*Zazo et al., 2006*
Cu	carbón activado	fenol	$C_{cont-cat-H2O2}$=1 - 2 - 3,4 g/L T=80 ºC	$X_{cont,COT}$=100%, 90% (t=20 min)	-	*Liou y Chen., 2009*
Cu	carbón activado	naftalina	$C_{cont-cat-H2O2}$=1 - 2 - 34 g/L T=100 ºC, P=20 atm, pH=2	X_{cont}=100% (t=30 min)	$Cu_{lixiviado}$=17 mg/L	*Onda et al., 2008*
Cu	carbón activado	fenol	$C_{cont-cat-H2O2}$=1 - 1 - 5 g/L T=35 ºC, P=1 atm, pH=6,5	$X_{cont,DQO}$=100%, 80% (t=360 min)	$Cu_{lixiviado}$=10 mg/L	*Britto et al., 2008*
Mn	carbón mesoporoso con estructura hexagonal	fenol	$C_{cont-cat}$=0,1 - 2 g/L, 2*H_2O_2 esteq. T=60 ºC, P=1 atm, pH=5,8	X_{cont}=95% (t=360 min)	estable 20 usos consecutivos	*Kong et al., 2012*
Ni	aerogel de carbón	colorante	$C_{cont-H2O2}$=0,1 - 6 mM, C_{cat}=0,2 g/L T=30 ºC, P=1 atm, pH=3	X_{cont}=40% (t=24 h)	$Ni_{lixiviado}$=0,03 mg/L (1%)	*Duarte et al., 2009*
Co	aerogel de carbón	colorante	$C_{cont-H2O2}$=0,1 - 6 mM, C_{cat}=0,2 g/L T=30 ºC, P=1 atm, pH=3	X_{cont}=65% (t=24 h)	$Co_{lixiviado}$=1 mg/L (25-30%)	*Duarte et al., 2009*
Co	fibras carbón activado	4-nitrofenol	$C_{cont-cat-H2O2}$=0,05 - 2 - 3,4 g/L T=25 ºC, P=1 atm, pH=6,8	$X_{cont,COT}$=95%, 90% (t=5 h) imp. contribución adsorción (60%)	puede reutilizarse	*Lu et al., 2009*

Fase activa	Soporte	Contaminante	Condiciones operación	Resultados	Estabilidad	*Referencia*
Au	carbón activado	bis-fenol A	$C_{cont\text{-}cat\text{-}H2O2}$=0,114 - 0,125 - 0,53 g/L T=40 ºC, P=1 atm, pH=3	X_{cont}=90% (t=12 h)	desactivación por adsorción de sub-productos de reacción	*Yang et al., 2013*
Au	diamante	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 1 - 0,2 g/L T=50 ºC, P=1 atm, pH=4	X_{cont}=100% (t=5 h)	no lixiviación de Au desactivación por adsorción de ácidos carboxílicos sobre Au. regeneración: lavado a pH básico	*Martin et al., 2011*
Au	carbón activado	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,1 - 16,5 g/L (exceso) T=70 ºC, P=1 atm, pH=6,8	X_{cont}=19% (t=2 h)		*Han et al., 2008*
Cr	carbón activado	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,01 - 1 - 3,4 g/L T=25 ºC, P=1 atm, pH=6	X_{COT}=60% (t=60 min)	$Cr_{lixiviado}$=46 mg/L	*Oliveira et al., 2011*

C_{cont}=concentración de contaminante, C_{cat}=concentración de catalizador, C_{H2O2}=concentración de peróxido de hidrógeno, $X_{cont,}$ $X_{cont\ CWPO}$ = conversión de contaminante por oxidación, X_{COT} = conversión de carbón orgánico total, X_{DQO}= conversión de demanda química de oxígeno, X_{ads} = eliminación de contaminante por adsorción

Tabla 3.5. Tipo de material carbonoso empleado como catalizador del proceso CWPO, tipo de contaminante tratado, condiciones de operación empleadas y resultados más relevantes.

Material carbonoso	Contaminante	Condiciones de operación	Resultados	Estabilidad	Referencia
carbón activado	2-nitrofenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,1 - 1,2 g/L (exceso) T=50 ºC, P=1 atm, pH=3	$X_{cont\ CWPO,\ ads}$=30%, 30% (t=150 min)	-	Ribeiro et al., 2013
carbón activado con propiedades magnéticas	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,3 - 0,15 - 0,5 g/L T=25 ºC, P=1 atm, pH=5	$X_{cont,COT,ads}$=94%, 48, 40% (t=10 h) (impurezas Fe)	$Fe_{lixiviado}$=0,78 mg/L (1,5%)	Gu et al., 2013
carbón activado	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,2 - 2,2 - 34 g/L (exceso) T=25 ºC, P=1 atm, pH=3,5	$X_{cont\ CWPO,\ ads}$=65%, 40% (t=180 min)	-	Soria-Sánchez et al., 2012
carbón activado	colorante	$C_{cont\text{-}cat}$=0,1 - 0,5 C_{H2O2}=5*esteq T=50 ºC, P=1 atm, pH=3	$X_{cont\ CWPO,\ ads}$=35%, 10% (t=150 min)	-	Gomes et al., 2011
carbón activado	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,2 - 0,5 - 2,2 g/L T=80 ºC, P=1 atm, pH=3	$X_{cont\ CWPO,\ ads}$=93%, 60% (t=120 min)	-	Türgay et al., 2011
carbón activado	colorante	$C_{cont\text{-}H2O2}$=0,1 - 6 mM, C_{cat}=0,1 g/L T=30 ºC, P=1 atm, pH=3	X_{color}=90% (24 h), carbón presaturado	-	Duarte et al., 2011
carbón activado	herbicida	$C_{cont\text{-}cat}$=0,02 - 0,25 g/L, C_{H2O2}=1-5*esteq T=30-70 ºC, P=1 atm	X_{DQO}=71% (1 g/L cat, 70 ºC) (180 min) (contribución importante adsorción)	-	Dhaouadi et al., 2010
carbón activado	colorante	$C_{cont\text{-}cat}$=0,1 - 0,5, C_{H2O2}=5*esteq T=50 ºC, P=1 atm, pH=3	$X_{cont\ CWPO,\ ads}$=35%, 10% (t=150 min)	pierde actividad de 1er a 2º uso (debido a adsorción)	Gomes et al., 2010
carbón activado	fenol	$C_{cont\text{-}cat}$=1 - 4 g/L, C_{H2O2}=continuo (1,3 mM/min, exceso) T=70 ºC, P=1 atm, pH=5,5	$X_{cont\ CWPO,\ ads}$=100%, 35% (t=180 min)	-	Dehkordi y Ebrahimi., 2009
carbón activado	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,01 - 2,15 - 51 g/L (exceso) T=25 ºC, P=1 atm, pH=3	$X_{color,\ ads}$=70%, 22% (t=180 min)	-	Santos et al., 2009

Material carbonoso	Contaminante	Condiciones de operación	Resultados	Estabilidad	Referencia
carbón activado	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,5 - 0,5 g/L T=50 ºC, P=1 atm, pH=3	$X_{COT,\ ads}$=70%, 55% (t=60 min) (cenizas de Fe)	-	Rey et al., 2008
carbón activado	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,5 - 0,5 g/L T=50 ºC, P=1 atm, pH=3	$X_{cont\ CWPO,\ ads}$=55%, 52% (t=60 min) (contribución importante de adsorción)	-	Zazo et al., 2006
carbón activado	MTBE TCP	$C_{cont\text{-}H2O2}$=1 - 67 mM, C_{cat}=1 g/L T=23 ºC, P=1 atm, pH=3	X_{MTBE}= 100% (t=5 h), carbón presaturado X_{TCP}= 100% (t=300 h), carbón presaturado (contribución de adsorción)	-	Georgi and Kopinke, 2005
carbón activado	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,05 - 6 – 100 g/L (exceso) pH=6	$X_{cont\ CWPO,\ ads}$=99%, 44% (t=240 min)	-	Oliveira et al., 2004
carbón activado	4-clorofenol	$C_{cot\text{-}cat\text{-}H2O2}$= 0,15 - 1 - 0,7 g/L (exceso) T=30ºC, P=1 atm, pH=7	X_{cont}=60% (t=25 min)	-	Huang et al., 2003
carbón activado	4-clorofenol	$C_{cont\text{-}cat}$=1 - 1 g/L, C_{H2O2}=1,5*esteq T=30 ºC, P=1 atm, pH=3	X_{DQO}=45% (t=200 h)	$Fe_{lixiviado}$=1 mg/L	Lücking et al., 1998
grafito de alta superficie	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,2 - 2,2 - 34 g/L (exceso) T=25 ºC, P=1 atm, pH=3,5	Xcont CWPO, ads=55%, 40% (t=180 min)	-	Soria-Sánchez et al., 2012
grafito mesoporoso	fenol etanol ácido fórmico	$C_{cont\text{-}H2O2}$=0,01 - 0,1; 0,06 - 0,5 mM, C_{cat}=5 g/L T=30 ºC, P=1 atm, pH=3	X_{fenol}=75% (100 h) X_{etanol}<10% (100 h) $X_{ácido\ fórmico}$=90% (400 h)	-	Taran et al., 2010
grafito poroso	fenol	$C_{cont\text{-}cat\text{-}H2O2}$=1 - 5 - 3,4 g/L T=90 ºC	$X_{cont\ (1,2\ usos)}$=86%, 77% (180 min)	Pierde actividad con los usos	Pestunova et al., 2003
grafito	4-clorofenol	$C_{cont\text{-}cat}$=1 - 1 g/L, C_{H2O2}=1,5*esteq T=30 ºC, P=1 atm, pH=3	X_{DQO}=30% (t=100 h)	$Fe_{lixiviado}$=1 mg/L	Lücking et al., 1998

Material carbonoso	Contaminante	Condiciones de operación	Resultados	Estabilidad	Referencia
nanotubos de carbono	2-nitrofenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,1 - 1,2 g/L T=50 ºC, P=1 atm, pH=3	$X_{cont\ CWPO,\ ads}$ =94%, 11% (t=150 min)	$Fe_{lixiviado}$=0,02 mg/L	Ribeiro et al., 2013
nanotubos de carbono	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,2 - 2,2 - 34 g/L (exceso) T=25 ºC, P=1 atm, pH=3,5	$X_{cont\ CWPO,\ ads}$ =100%, 75% (t=180 min)	-	Soria-Sánchez et al., 2012
xerogel de carbón activado	2-nitrofenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,1 - 1,2 g/L (exceso) T=50 ºC, P=1 atm, pH=3	$X_{cont\ CWPO,\ ads}$ =22%, 27% (t=150 min)	-	Ribeiro et al., 2013
xerogel de carbón activado	colorante	$C_{cont\text{-}cat}$=0,1-0,5 C_{H2O2}=5*esteq T=50 ºC, P=1 atm, pH=3	$X_{cont\ CWPO,\ ads}$=60%, 25% (t=150 min)	pierde actividad de 1er a 2º uso después estable	Ribeiro et al., 2012
nanofibras de carbono	colorante	$C_{cont\text{-}cat\text{-}H2O2}$=0,2 - 2,2 - 34 g/L (exceso) T=25 ºC, P=1 atm, pH=3,5	$X_{cont\ CWPO,\ ads}$ =35%, 22% (t=180 min)		Soria-Sánchez et al., 2012
carbón basado en glicerol	2-Nitrofenol	$C_{cont\text{-}cat\text{-}H2O2}$=0,1 - 0,1 - 1,2 g/L (exceso) T=50 ºC, P=1 atm, pH=3	$X_{cont\ CWPO,\ ads}$ =63%, 7% (t=150 min)		Ribeiro et al., 2013
carbón filamentoso	fenol etanol ácido fórmico	$C_{cont\text{-}H2O2}$=0,01 - 0,1; 0,06 - 0,5 mM, C_{cat}=5 g/L T=30 ºC, P=1 atm, pH=3	X_{fenol}=98% (720 h) X_{etanol}=95% (100 h) $X_{ácido\ fórmico}$=90% (200 h)	-	Taran et al., 2010
carbón tipo cebolla	fenol etanol ácido fórmico	$C_{cont\text{-}H2O2}$=0,01 - 0,1; 0,06 - 0,5 mM, C_{cat}=5 g/L T=30 ºC, P=1 atm, pH=3	X_{fenol}=35% (200 h) X_{etanol}=100% (80 h) $X_{ácido\ fórmico}$=65% (220 h)	-	Taran et al., 2010
nanodiamantes	fenol etanol ácido fórmico	$C_{cont\text{-}H2O2}$=0,01 - 0,1; 0,06 - 0,5 mM, C_{cat}=5 g/L T=30 ºC, P=1 atm, pH=3	X_{fenol}=85% (650 h) X_{etanol}<10% (100 h) $X_{ácido\ fórmico}$=20% (400 h)	-	Taran et al., 2010

C_{cont}=concentración de contaminante, C_{cat}=concentración de catalizador, C_{H2O2}=concentración de peróxido de hidrógeno, $X_{cont,}$ $X_{cont\ CWPO}$ = conversión de contaminante por oxidación, X_{COT} = conversión de carbón orgánico total, X_{DQO}= conversión de demanda química de oxígeno, X_{ads} = eliminación de contaminante por adsorción

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3

Objetivos

El objetivo de la presente Tesis Doctoral es la obtención de catalizadores basados en materiales carbonosos, activos, eficientes y estables para su empleo en el tratamiento de aguas residuales contaminadas por compuestos orgánicos resistentes a la biodegradación mediante oxidación húmeda catalítica con peróxido de hidrógeno.

Dado este objetivo, se va a analizar el papel del carbón activado como soporte catalítico y como catalizador de dicho proceso. En este último caso, se estudiará también el empleo de otro tipo de materiales carbonosos, como negros de humo y grafitos. Para ello, se emplearán aguas residuales sintéticas, contaminadas por compuestos modelo, y aguas residuales industriales, procedentes de la industria vitivinícola.

El interés de un catalizador heterogéneo reside en su capacidad para aumentar la velocidad de reacción del proceso, la fácil separación del mismo del medio de reac-

ción y su reutilización. Los catalizadores heterogéneos empleados en la oxidación húmeda con peróxido de hidrógeno deben catalizar la reacción de descomposición de este oxidante a especies radicalarias, así como promover la posterior reacción de oxidación entre los radicales formados y la materia orgánica, de modo que se obtengan elevados grados de oxidación y mineralización, y, por lo tanto, se alcance un consumo eficiente de peróxido de hidrógeno. El principal inconveniente de los catalizadores existentes es su baja estabilidad, debida, principalmente, a la lixiviación de la fase activa al efluente de reacción, lo que, en ocasiones, provoca un problema de contaminación adicional, y/o en menor medida, a la presencia de depósitos carbonosos sobre la superficie del catalizador. Todo ello dificulta o imposibilita su reutilización.

Por tanto, para evaluar la idoneidad de catalizadores basados en materiales carbonosos en la oxidación húmeda con peróxido de hidrógeno se estudiarán los siguientes aspectos:

i) **Capacidad oxido-reductora** de los catalizadores, para poder predecir su actividad catalítica en la reacción de descomposición de peróxido de hidrógeno a especies radicalarias.

ii) **Actividad catalítica** en las reacciones de oxidación y mineralización de contaminantes orgánicos persistentes.

iii) **Eficiencia en el consumo de peróxido de hidrógeno**, determinada como la cantidad de materia orgánica mineralizada por unidad de peróxido de hidrógeno consumido.

iv) **Estabilidad** y reutilización de los catalizadores.

Hay que destacar que, aunque existen numerosos trabajos en la literatura sobre oxidación húmeda catalítica con peróxido de hidrógeno, apenas se hace referencia a los aspectos iii) e iv) anteriormente citados.

Para la consecución del objetivo principal, el trabajo desarrolla los siguientes objetivos parciales:

1. Empleo de carbón activado como soporte de metales resistentes a la lixiviación, como es el oro. Las propiedades redox de este metal, en particular, los potenciales de oxidación y reducción del mismo, le confieren una alta actividad en la reacción de descomposición de peróxido de hidrógeno a radicales hidroxilo e hidroperóxido. Este hecho, unido a las adecuadas propiedades físico-químicas de los carbones activados para su empleo como soportes catalíticos, hacen que el catalizador de nanopartículas de oro soportadas sobre carbón activado (Au/CA) sea de especial interés en procesos de oxidación húmeda con peróxido de hidrógeno.

2. Uso de materiales carbonosos, viz. carbones activados, negros de humo y grafitos, como catalizadores en procesos de oxidación húmeda con peróxido de hidrógeno. Gracias a su química superficial, consecuencia de la presencia de grupos superficiales oxigenados, planos basales del carbón y cenizas metálicas, estos materiales presentan propiedades superficiales oxido-reductoras que les permite actuar como catalizadores en la reacción de descomposición de peróxido de hidrógeno.

3. Aplicar el proceso de oxidación húmeda con peróxido de hidrógeno en presencia de catalizadores basados en materiales carbonosos (seleccionados en los estudios anteriores) en el tratamiento de aguas residuales industriales, en particular, de aguas procedentes de la industria vitivinícola.

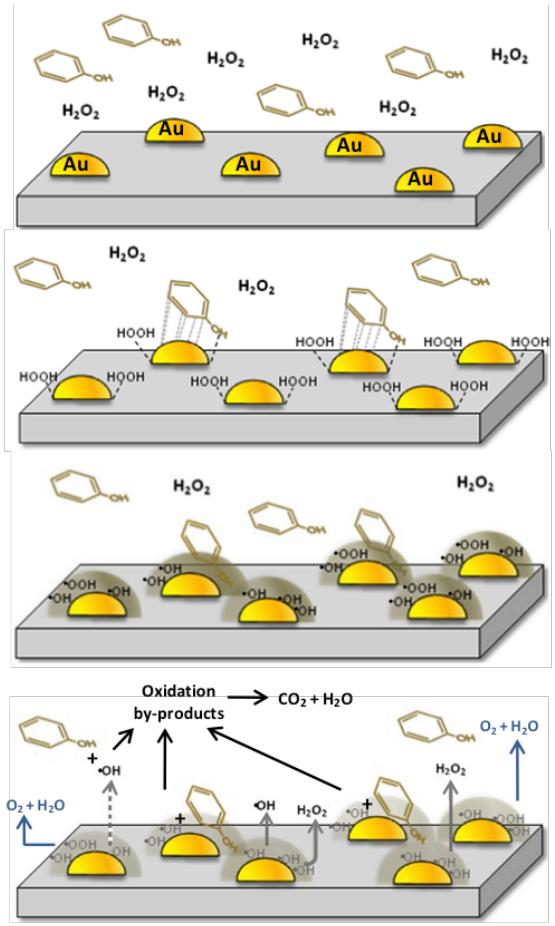
4

Resultados y Discusión

Bloque I

Catalizadores de oro soportado sobre carbón activado para procesos de oxidación húmeda con peróxido de hidrógeno

Capítulo I. Supported gold nanoparticle catalyst for wet peroxide oxidation



Applied Catalysis B: Environmental 111–112 (2012) 81–89

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Supported gold nanoparticle catalysts for wet peroxide oxidation

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ARTICLE INFO

Article history:
Received 17 May 2011
Received in revised form 8 September 2011
Accepted 19 September 2011
Available online 24 September 2011

Keywords:
Gold
Nanoparticle
Hydrogen peroxide
Catalytic wet oxidation
Oxidation pathway

ABSTRACT

Supported gold nanoparticles are of promising interest in wet hydrogen peroxide oxidation processes due to their efficient hydrogen peroxide consumption and adequate stability. Here, the origin of the catalytic properties of gold in this environmental process is explored by analyzing the influence of the support and the particle size on the activity of supported gold nanoparticles along with the influence of the nature of the target pollutant on the gold reactivity. The reaction mechanism for the oxidation of phenol with activated carbon-supported gold nanoparticles is proposed and the selectivity evaluated. A reaction pathway has been also proposed.

The results demonstrate that wet peroxide oxidation is a support and gold size dependent reaction. Activated carbon is the preferable candidate *versus* TiO_2 and Fe_2O_3 supports and small gold nanoparticles, desirably lower than 3 nm, show the highest TOF values. Supports showing adsorption capacity towards the target pollutant contribute to a more efficient use of hydrogen peroxide and, improve the TOF values for the oxidation and mineralization. Organic pollutants forming intermediate complexes with gold, *viz.* alcohols, are more efficiently oxidized. The inclusion of gold improves substantially the selectivity towards mineralization with respect to the bare activated carbon.

1. Introduction

The catalytic wet peroxide oxidation (CWPO) process relies on the oxidation of suspended or diluted organic matter in water under mild operating conditions (T = 298–383 K, P = 1–5 atm) using hydrogen peroxide as oxidant. The main active species for the oxidation is the hydroxyl radical, produced from hydrogen peroxide decomposition catalyzed by iron. The system $H_2O_2 + Fe^{2+}$ is the well-known Fenton reagent [1,2]. The current commercial units (US Peroxide, OXY-PURE®, OHP® and PROX T.E.C) are based on this catalytic system because of the operational simplicity and low-cost in comparison with other advanced oxidation processes [3]. However, it also presents several drawbacks derived from the operating pH (which must be maintained around 3, [4]), loss of iron with the consequent production of iron waste sludge and catalytic inhibition upon iron sequestering by-some of the reaction by-products giving rise iron-organic complexes [5,6]. These problems can be diminished by the immobilization of the iron on a support, *i.e.* alumina [7,8], silica [9,10], mesoporous silica [11–15], pillared clays [16–20], zeolites [21–25], activated carbon [26–29], carbon aerogels [30,31] and carbon nanotubes [32].

Unfortunately, these iron-heterogeneous systems show other different drawbacks derived from the low-efficient consumption of hydrogen peroxide, since some supports such as activated carbons can contribute to the inefficient decomposition of hydrogen peroxide into oxygen [33]. The poor stability of the catalysts, caused by iron leaching, is also a matter of concern [4,5,10,27,28,14]. In this sense, gold has recently shown its supremacy. The novel work of Han et al. [34], presented gold as active catalysts in wet peroxide oxidation processes, demonstrating the superior stability of gold-on-hydroxyapatite over Fe/ZSM-5 catalyst in the treatment of low-polluted wastewater (*i.e.* 0.1 g/L organic contaminant such as phenol). Later, Quintanilla et al. [35], demonstrated the use of gold catalysts also for medium-loaded wastewater (*i.e.* 1–5 g/L phenol). In that work, the presence of hydroxyl radicals was proved, by using a selective quencher, and a reaction mechanism was proposed based on the redox cycle accomplished between Au^0 and Au^+ species:

$$Au^0 + H_2O_2 \rightarrow HO^\bullet + HO^- + Au^+ \quad (1)$$

$$Au^+ + H_2O_2 \rightarrow {}^\bullet OOH + H^+ + Au^0 \quad (2)$$

Recently, the work of Martín et al. [36], working with gold-on-nanosized diamond prepared in a previous work [37], demonstrated that small gold nanoparticles (sizes lower than 1 nm) supported on diamond nanoparticles are an efficient catalyst in the sense of achieving adequate biodegradability of phenolic wastewater with values of H_2O_2 to phenol molar ratio as low as 4, which is

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doi:10.1016/j.apcatb.2011.09.020

6.5 times lower than the theoretical stoichiometric amount of H_2O_2 usually employed for complete phenol oxidation (mineralization).

Herein, an insight into the origin of the catalytic properties of gold in wet peroxide oxidation is accomplished. The influence of the nature of the support and the size of gold particles deposited on a support have been explored along with the effect of the nature of the pollutant on the gold reactivity. Experimental work on small gold particles immobilized on different supports (TiO_2, C and Fe_2O_3) used in the oxidation of two different target compounds (*viz.* phenol and benzyl alcohol) has been performed along with an study of the catalytic behavior of size-selected gold particles deposited on activated carbon in the wet peroxidation of phenol. The results have been analyzed in terms of conversions, initial rates and Turn-over-Frequencies (TOFs) and supported with TEM and XPS analyzes. The reaction mechanism for the oxidation of phenol with activated carbon-supported gold nanoparticles is proposed and the selectivity evaluated. A reaction pathway has been also proposed.

2. Experimental

2.1. Catalysts

0.8 wt%·Au/TiO_2 (Mintek, batch: BC14) and 4.5 wt%·Au/Fe_2O_3 (Word Gold Council) catalysts were used as-received. In addition, size-selected Au/C catalysts (C is an activated carbon supplied by Merck, Ref.: 102514, $S_{BET} = 973\ m^2/g$, $A_{ext} = 175\ m^2/g$, $V_{micro} = 0.38\ cm^3/g$) were prepared in our lab by the gold-sol immobilization method. Different aqueous gold colloids were used: 3 nm citrate-capped gold (Strem Chemicals Inc.) and 5.1 ± 0.7, 7.2 ± 0.5 and 9.8 ± 1.4 nm tannic acid-capped gold nanoparticles (Nanocomposix). The appropriate volume of the spherical-shape particles suspension was stirred overnight with the corresponding mass of carbon in order to obtain the targeted content of gold of 0.5 wt%. The red colour of the colloid solution faded overnight indicating the removal of gold from the aqueous phase; carbon did not apparently change in colour. After stirring, the suspension was dried at 333 K until complete evaporation of the remaining solution. The resulting Au/C catalyst was subsequently washed with water and dried. The catalysts are designated as Au(3)/C, Au(5)/C, Au(7)/C and Au(10)/C according to the original average size (nm) of gold in the colloid.

The gold content of the catalysts was determined by ICP (Elan 6000 PerkinElmer Sciex) and confirmed by fluorescence spectroscopy (Si–Li detector in a TXRF Extra-II Rich & Seifert spectrometer). The gold particle size distribution was obtained with a 200 kV JEM-2100F transmission electron microscope (JEOL Ltd.) by observation of several micrographs taken from different regions of the particular catalysts. In the case of Au/TiO_2 catalyst, small crystalline gold particles were not clearly distinguished from crystalline TiO_2. Then, the observation of this sample was performed in scanning mode and recorded with an annular dark field detector with an inner detection angle of 68.5 mrad (HAADF-STEM). The contrast in this mode is a function of atomic number, which enabled the straight gold particle observation.

The exposed gold surface species (Au^0, $Au^{\delta+}$) were quantified by XPS. Spectra were recorded using a VG Escalab 200R electron spectroscope equipped with a hemispherical analyzer, operating in a constant pass energy mode and a non-monochromatic Mg Kα ($h\nu = 1253.6$ eV, $1\ eV = 1.603 \times 10^{-19}$ J). X-ray source operated at 10 mA and 12 kV. The energy regions of the photoelectrons of interest were scanned a number of times in order to get good signal-to-noise ratios. The intensities of the peaks were estimated by calculating the integral of each peak after subtracting a Shirley type background and fitting the experimental peak to a combination of Lorenzian/Gaussian lines of variable proportions. The binding energies (BE) were referenced to the C1s peak (284.6 eV).

2.2. Wet peroxide oxidation experiments

The oxidation tests were carried out batch-wise in a magnetically stirred three-necked glass reactor equipped with a reflux condenser. In a typical experiment, 45 mL of distilled water containing 5 g/L of phenol or benzyl alcohol (Sigma–Aldrich) at pH 3.5 (HCl, Sigma–Aldrich) was placed in the flask, along with 0.125 g of catalyst. This acidic pH was selected in order to work within the range of pH values used in heterogeneous Fenton process, in which some leaching of Fe is usually observed. Then, the reaction content was heated to 353 K (IKA RCT basic). Once this temperature was reached, 5 mL of an adjusted concentration of hydrogen peroxide (Sigma–Aldrich) was injected and the stirring at 1200 rpm started. After 24 h of reaction, the heating and stirring were switched-off and the flask cooled to room temperature by soaking in a crushed ice bath. Then the catalyst was separated by filtration (0.45 μm Nylon filter) and oven-dried at 333 K. All the gold-on-carbon catalysts used in reaction were previously treated in order to avoid the adsorption contribution to the overall phenol and TOC uptake and to enable the catalytic activity comparison to the others supported gold catalysts. The pre-treatment consisted of washing the catalyst in a phenol solution at the same operating conditions as the oxidation tests but in absence of hydrogen peroxide during 24 h. Also, adsorption runs were performed with Au/TiO_2 catalyst for each target compound (phenol and benzyl alcohol) in order to study the influence of the nature of the pollutant on the gold reactivity. Additionally, some experiments were performed at a lower stirring rate (200 rpm in an orbital shaker, Julabo, SW22) to confirm the absence of external mass transfer limitations. The particle size employed ($d_p < 80$ μm) also assures the absence of internal diffusion limitations (Thiele modulus around 3×10^{-3}, based on the observed initial phenol oxidation rate of the Au(3)/C catalyst). The homogenous contribution was assessed by working in absence of catalyst.

0.5 mL-samples were periodically collected by a syringe, and immediately injected in a vial, submerged in crushed ice, containing cold milliQ water. The diluted samples were subsequently filtered and analyzed by different techniques. Phenol, benzyl alcohol and aromatic by-products were identified and quantified by HPLC (Varian Pro-Start 240) and low molecular weight acids by IC with anionic chemical suppression (Metrohm, mod. 761 Compact IC). Detailed operational conditions of these techniques have been reported elsewhere [38]. TOC was measured in a TOC analyzer (Shimadzu TOC V_{SCH}). Hydrogen peroxide concentration was quantified by colorimetric titration using the titanium sulfate method. The efficiency of hydrogen peroxide consumption is given by the ratio of TOC to hydrogen peroxide conversions. A value equal to 1 means the best achievement according to the stoichiometric amount of hydrogen peroxide used in all the experiments. Metal content in the liquid effluents was determined by TXRF (Extra-II Rich & Seifert spectrometer). The presence of hydroxyl radicals was visualized by the methylene blue dye test. Effluents at different reaction times were drop-sampled on a blue methyl tip prepared according to Satoh et al. protocol [39]. The decolorization of the tip corresponds to the oxidation of the methylene blue dye (dark blue colour) to methyl blue radical cation (colourless) by the hydroxyl radicals.

Table 1
Gold loading, particle size and percentage of exposed surface gold species of the catalysts tested and their preparation method.

Catalyst	$[Au]_{total}$ (wt %)	Au_p (nm)	Au^0 fraction (%)	$Au^{\delta+}$ fraction (%)	Au/M[a]	Preparation method
Au/TiO_2	0.80	3.1 ± 1.8	79	21	0.014	Co-precipitation
Au/Fe_2O_3	4.48	3.6 ± 0.9[b]	26	74	0.045	Co-precipitation
Au(3)/C	0.13	5.1 ± 2.0[c]	69	31	0.002	Citrate-capped-gold immobilization
Au(5)/C	0.47	4.9 ± 1.0	72	28	0.004	Tannic acid-capped-gold immobilization
Au(7)/C	0.48	6.8 ± 1.7	71	29	0.025	Tannic acid-capped-gold immobilization
Au(10)/C	0.50	9.1 ± 1.1	69	31	0.015	Tannic acid-capped-gold immobilization

[a] M represents Ti, Fe or C, as corresponds.
[b] Data provided by the supplier, WGC.
[c] Two modes centered at 3.2 and 5.7 nm.

3. Results and discussion

3.1. Catalyst characterization

Table 1 summarizes the average gold particle sizes obtained from TEM. Some representative micrographs and the particle size distributions can be seen in Fig. 1. The commercial catalysts, Au/TiO_2 and Au/Fe_2O_3, contain spherical particles of around 3 nm. With respect to the gold-on-carbon catalysts, the spherical morphology and the particle size of the initial colloidal gold were maintained after immobilization on the activated carbon with the exception of the 3 nm citrate-capped gold particles (Table 1). In this case, a bimodal distribution, centered at 3.2 and 5.7 nm was found which leads to an average particle size of 5.1 ± 2.0 nm. This

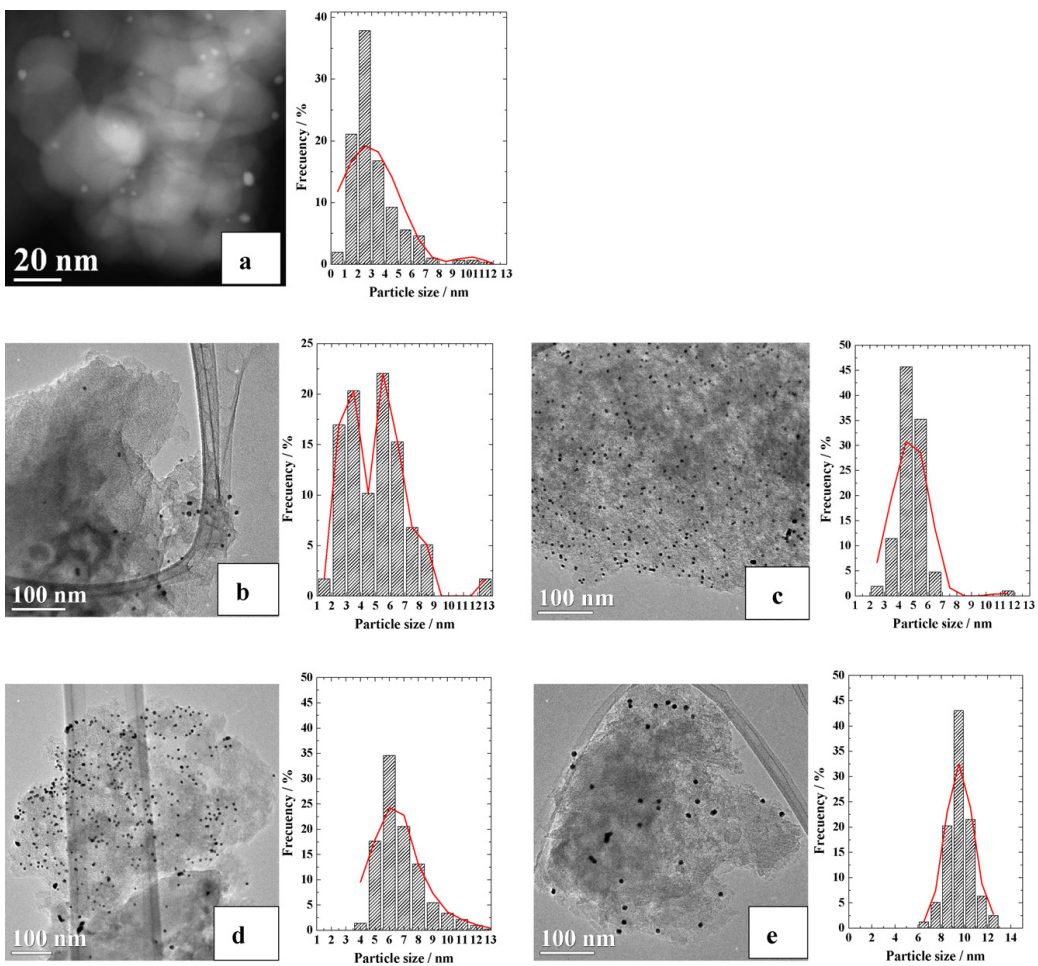

Fig. 1. HAADF-STEM (a) and TEM micrographs and particle size distributions corresponding to 0.8 wt.% Au/TiO_2 (a), 0.13 wt.% Au(3)/C (b), 0.5 wt.% Au(5)/C (c), 0.5 wt.% Au(7)/C (d), 0.5 wt.% Au(10)/C samples (e).

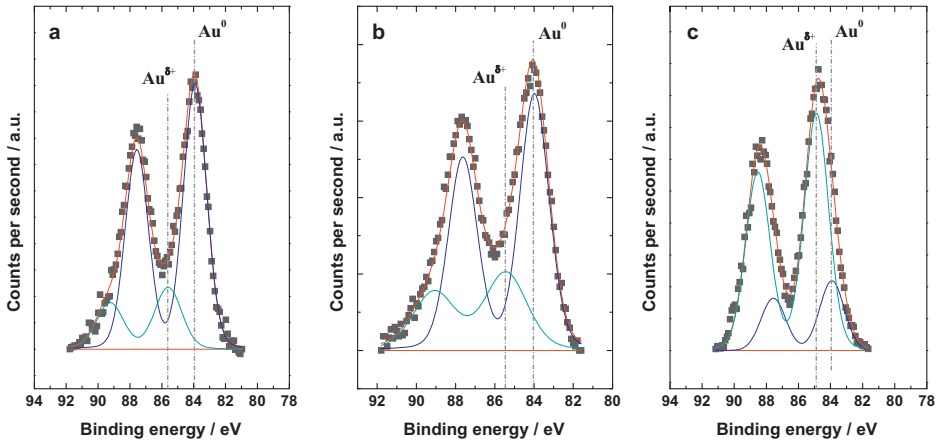

Fig. 2. Au 4f core level of XPS spectra of the Au/TiO_2 (a), Au(3)/C (b) and Au/Fe_2O_3 catalysts.

Au(3)/C is the gold-on-carbon catalysts containing the highest proportion of smaller gold particles and it will be selected for studying the effect of the nature of the support (TiO_2, Fe_2O_3 and C). The gold contents measured by ICP are also summarized in Table 1. The targeted 0.5 wt% was confirmed in the tannic acid-immobilized gold catalysts (Au(5)/C, Au(7)/C and Au(10)/C). However, citrate-immobilized gold catalyst (Au(3)/C), yielded only 0.13 wt% gold. This different behavior can be ascribed to the nature of the capping agent, in particular, the molecular structure and acid/basic properties. Regarding the structure, sodium citrate ($NaC_6H_7O_7$) as well as tannic acid ($C_{76}H_{52}O_{46}$) contain oxygen, which is the heteroatom bound to gold. However, different particle architecture is expected. Citrate anion is a small molecule adsorbed on the gold surface forming a self-assembled layer [40] whereas tannic acid is a rigid polymer conforming a gold core-porous shell that provides a better stability of the particle during the immobilization process and can guarantee the particle size conservation. Regarding the acid/basic properties, capping agents induce the pH of the colloidal gold sols that will affect the adsorption capacity of the carbon. The citrate gold sol has a pH of 8 and the carbon a pH at the point of zero charge of 7, therefore, the carbon surface is negatively charged and will repel the citrate anions. Then, the fade of the red colour of the sol during the preparation of this catalyst was caused by the preferential gold coating on the beaker surface, as confirmed by the ICP analysis of the wash-out of the beaker with aqua regia. In contrast, the acidic pH of the tannic acid-capped gold sols facilitates the adsorption of tannic acid on the carbon surface allowing a successful uptake of the targeted load for these series of catalysts.

Gold speciation, elemental composition in atom percent (at.%) and relative gold abundance (Au/M ratio, M being Ti, Fe or C, as corresponding) at the surface of the investigated catalysts, as obtained from the XPS analyzes, are also collected in Table 1. XPS spectra of the Au 4f core level and the binding energies of Au $4f_{7/2}$ photoelectrons can be seen in Fig. 2 and in Table S1 (Supporting Information), respectively. Au^0 and $Au^{\delta+}$ species were detected in all the catalysts. The binding energy of Au $4f_{7/2}$ photoelectrons in Au/TiO_2 and Au/C indicates that gold is present mainly as Au^0 (84.0 eV). A second gold species is observed at higher binding energies (85.5 eV) corresponding to electro-deficient gold ($Au^{\delta+}$). However, in the case of Au/Fe_2O_3, $Au^{\delta+}$ is the main exposed species. Therefore, the $Au^{\delta+}/Au^0$ surface ratio seems to be more dependent of the nature of the support than of the particle size. According to the Au/M ratio, gold is specially exposed in Au/Fe_2O_3.

3.2. Activity experiments

3.2.1. Support effect

The activity of gold nanoparticles can be strongly affected by the support, as observed with other gold-catalyzed processes [41–43]. To study this fact in the wet hydrogen peroxide oxidation, the catalytic activity of small gold particles, with an average particle size of around 3 nm, immobilized on different supports (TiO_2, C and Fe_2O_3), was studied. The results with phenol, after 4 h reaction time, are summarized in Fig. 3. As can be seen, hydrogen peroxide decomposition is promoted in presence of gold catalyst whereas the oxidation and mineralization of phenol is not always accordingly achieved. Au(3)/C and Au/Fe_2O_3 are active catalysts but Au/TiO_2 shows a moderate oxidation activity in spite of promoting a faster decomposition of hydrogen peroxide than Au(3)/C. The methylene blue test provided clear proof of the lower concentration of hydroxyl radicals in the liquid phase with Au/TiO_2 than with Au(3)/C (see Fig. S1 in the Supplementary information). Therefore, hydroxyl radicals produced in presence of Au/TiO_2 catalyst are mainly consumed in parasite reactions, yielding, for instance,

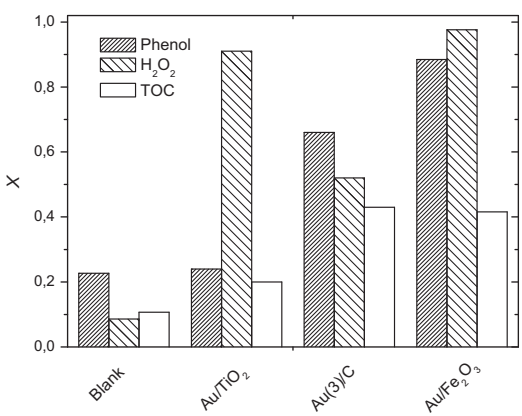

Fig. 3. Conversions achieved upon wet peroxide oxidation with gold nanoparticles on different supports after 4 h of reaction (C^0_{phenol} = 4.5 g/L, $C^0_{H_2O_2}$ = 22.5 g/L, C_{CAT} = 2.5 g/L, T = 353 K, p = 1 atm, pH_0 3.5).

Table 2
Initial rates and TOFs for hydrogen peroxide decomposition, phenol oxidation and mineralization.

Catalyst	r_o ($g_i/g_{solid}/h$)			$TOF_o \times 10^{-4}$ (h^{-1})		
	H_2O_2	Phenol	TOC	H_2O_2	Phenol	TOC
C	1.8	0.5	1.0	–	–	–
Au/TiO_2	17.0	1.3	1.0	2.52	0.07	0.07
Au(3)/C	13.5	2.7	2.0	16.70	1.19	1.08
Au(5)/C	10.3	2.2	1.5	4.07	0.32	0.25
Au(7)/C	4.4	1.4	1.1	2.27	0.25	0.25
Au(10)/C	2.9	2.0	1.5	1.87	0.47	0.43

Initial rates calculated as $(r_o)_i = (-dC_i/dt)_o \times 1/C_{CAT}$; TOFs (mol substrate/mol exposed gold/h). Mol exposed gold calculated assuming spherical nanoparticles and according to the particle size distribution derived by TEM.

oxygen and water, on the gold surface [35], instead of being released to the liquid phase where they could react with phenol molecules.

Leaching of gold was negligible (in the order of 0.01% of the initial gold load) whereas a significant concentration of iron was measured in the liquid phase from the experiments with the Au/Fe_2O_3 catalyst (73% of the initial iron was leached after 24 h of reaction). Thus, in the case of Au/Fe_2O_3, gold activity is masked by the significant homogeneous contribution caused by the dissolved iron. For this reason, and also considering the unlikely application of this unstable catalyst, Au/Fe_2O_3 was discarded for further studies.

The initial TOF values for hydrogen peroxide decomposition, phenol oxidation and mineralization (TOC) are summarized in Table 2 where the supremacy of Au(3)/C can be seen whereas Au/TiO_2 is by far the least active catalyst for phenol oxidation and mineralization. Noteworthy that in spite of the lower amount of gold particles with sizes equal or lower to 3 nm in Au(3)/C with respect to Au/TiO_2 (Fig. 1), as well as the lower proportion of Au^0 on the surface, the much lower exposition of gold (Au/M ratio values) (Table 1) and the presence of a capping agent (citrate), which may hinder the accessibility of the reactants to the active sites and/or act as catalyst surface poison [44], gold nanoparticles are clearly more active supported on carbon than on TiO_2. Interestingly, activated carbons are not inert supports and they usually exhibit activity in oxidation reactions [45]. Therefore, the Au(3)/C activity may consist on the contribution of both gold nanoparticles and carbon activity. To check this hypothesis, the activity of titania and carbon was explored at the selected operating conditions. The results demonstrated that only carbon (also previously contacted with a phenol solution) was active because hydrogen peroxide was decomposed on its surface and consequently phenol oxidation and mineralization took place. The initial rate values of carbon and Au(3)/C (Table 2) show the much lower activity of the former. The fact that 3 nm gold particles being much more active on carbon than on titania together with the low initial carbon activity suggest a synergistic effect between the gold particles and the carbon support. Considering the excellent adsorption properties of activated carbon, it is indeed tempting to assign this synergism to activated carbon-promoted or enhanced adsorption of phenol on gold nanoparticles. This adsorption of organic molecules on the gold surface can have two consequences: the decrease in the production of hydroxyl radicals by the partial occupation of the active sites by the organics and the increase of reacting chance between hydroxyl radicals and organics, both phenomena in detriment of the useless recombination and scavenging reactions of hydroxyl radicals. In both cases, a better use of the oxidant and high TOF values are obtained. In this sense, the use of supports with some adsorption capacity such as activated carbons and other modified carbonaceous materials is recommended.

According to the above discussion, a reaction mechanism for the oxidation of phenol on the carbon-supported gold nanoparticles has been proposed as shown in Fig. 4, where the following

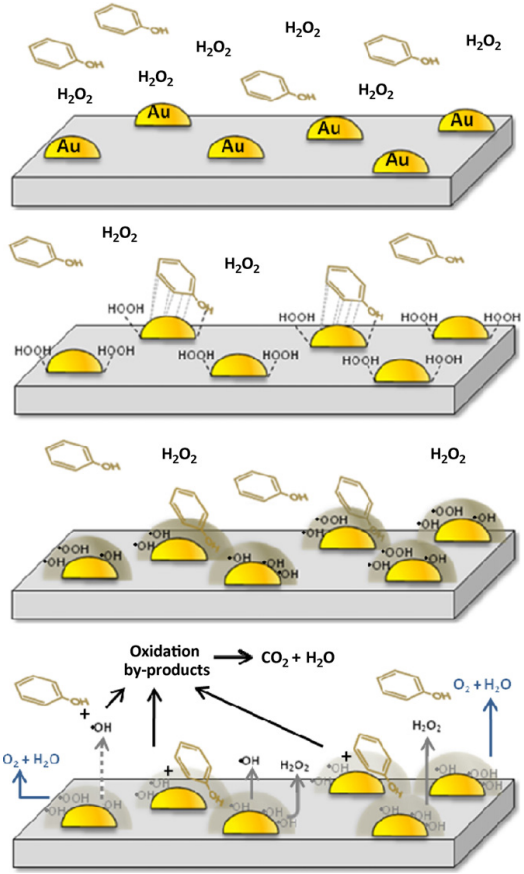

Fig. 4. Proposed mechanisms for phenol wet peroxide oxidation over carbon-supported gold nanoparticles.

steps are schematized: (i) adsorption of phenol and, preferentially, hydrogen peroxide on the gold-support interface, (ii) production of hydroxyl and hydroperoxyl radicals on the gold surface though some extension also occurs on the carbon surface and (iii) reactions between hydroxyl and phenol molecules on the gold surface. Also, hydroxyl radicals are released to the liquid phase where they react with phenol in solution. Parasite reactions, by the recombination of radicals species present, can take place yielding hydrogen peroxide and also oxygen and water.

3.2.2. *Gold particle size effect*

The particle size dependence of phenol oxidation was investigated by using gold particles of selected sizes immobilized on carbon, catalysts named Au(3)/C, Au(5)/C, Au(7)/C and Au(10)/C. The results in terms of initial rates and TOFs for hydrogen peroxide decomposition, phenol and TOC disappearance are summarized in Table 2. As a general trend, the lower the particle size the higher the TOF. This is especially evident for the catalytic decomposition of hydrogen peroxide where the highest TOF values are obtained. The size dependence becomes less significant in phenol oxidation and mineralization at gold particle sizes beyond 5 nm. We can anticipate that phenol diffusion hindrance could be expected with tannic acid but not with citrate shields [44], fact that can contribute to the

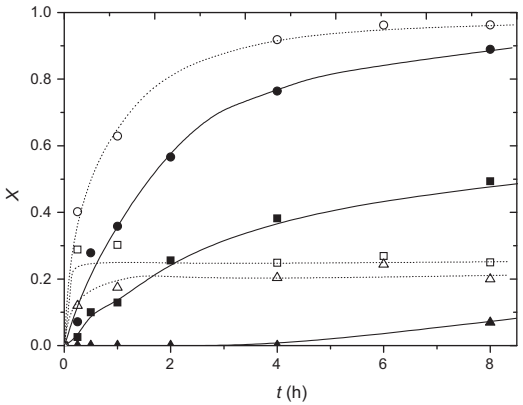

Fig. 5. Hydrogen peroxide (circle), target compound (squares) and TOC (triangles) conversions *vs.* reaction time upon phenol (dot line) and benzyl alcohol (solid line) wet peroxidation over Au/TiO_2 catalysts ($C^0_{pollutant} = 4.5$ g/L, $C^0_{H_2O_2}$ corresponding to the stoichiometric amount for mineralization of the pollutants, $C_{CAT} = 2.5$ g/L, $T = 353$ K, $p = 1$ atm, pH_0 3.5).

supremacy of the Au(3)/C catalyst and to moderate the particle size effect in the tannic acid-capped gold.

3.2.3. Effect of the target compound

The low phenol conversions observed with the Au/TiO_2 catalyst are in agreement with the results of Navalon et al. [37]. Interestingly, Ni et al. [46] achieved conversions of 90–99% in the selective oxidation of solvent-free aromatic and aliphatic alcohols with hydrogen peroxide; in that work, phenols were not tested. The low activity of gold in the wet peroxide oxidation of phenol could be ascribed to the nature of this compound. Phenols are less reactive than alcohols in gold–H_2O_2 systems. To understand this aspect, oxidation experiments have been carried out with Au/TiO_2 and benzyl alcohol as target compound. The conversion profiles (hydrogen peroxide, starting compound and TOC) with reaction time are given in Fig. 5. The results obtained with phenol have been also included for the sake of comparison. As observed, hydrogen peroxide is decomposed slowly in presence of benzyl alcohol and the oxidation of this alcohol takes place progressively. Benzyl alcohol is oxidized to aromatic by-products (benzaldehyde and benzoic acid) but mineralization only takes place after an induction period of several hours and reaches fairly low values along the 8 h of the experiment. A quite different scenario can be described for phenol since in this case, the initial oxidation of this compound is faster

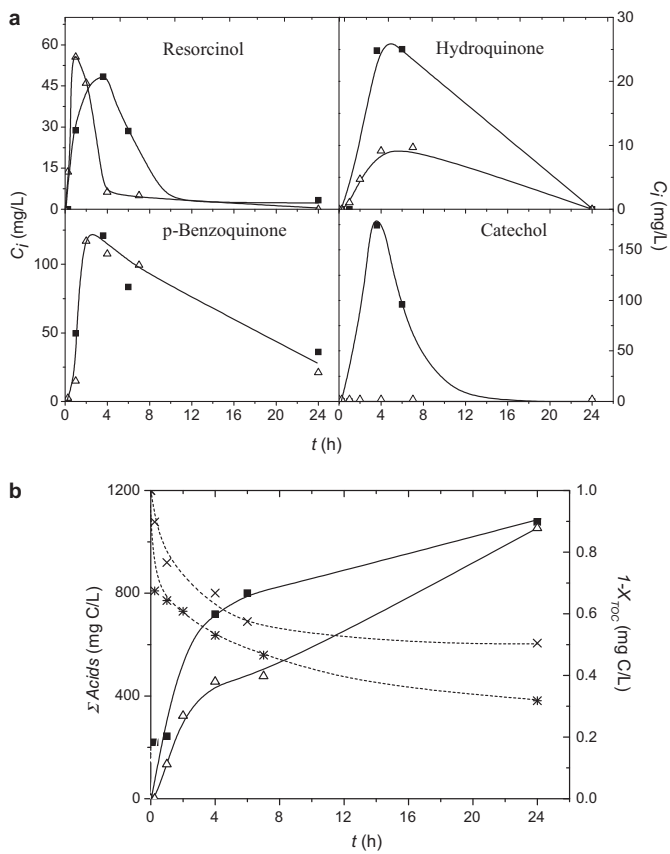

Fig. 6. Evolution of by-products and TOC removal from phenol peroxidation over Au(3)/C (open symbols and *) and bare activated carbon (closed symbols and ×) at the operating conditions of Fig. 3.

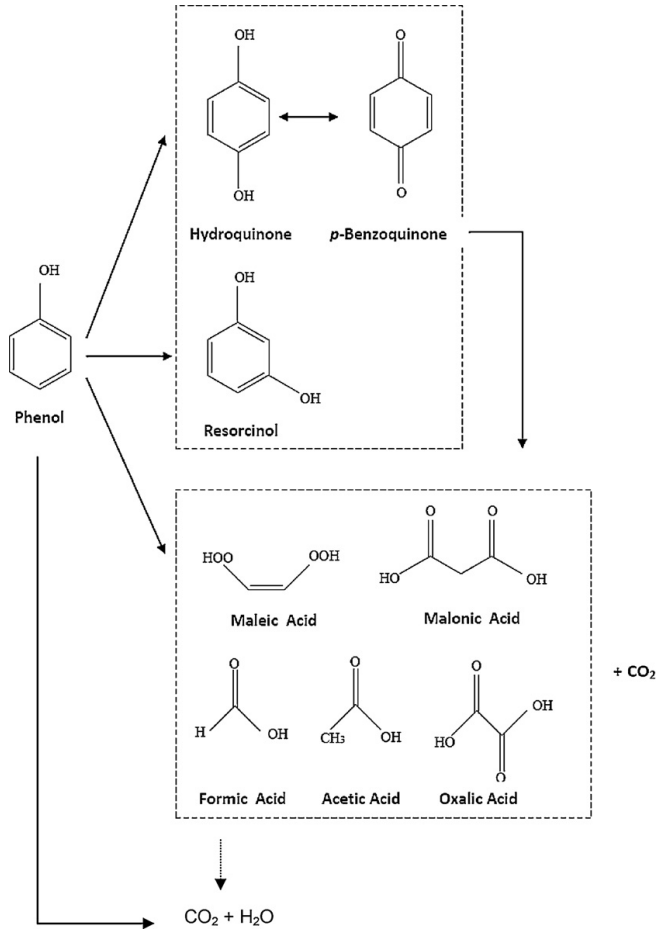

Fig. 7. Reaction pathway for wet peroxidation of phenol over gold on carbon nanoparticles.

than that of the alcohol but it stops after 0.5 h, though hydrogen peroxide is still decomposing on the gold surface. TOC reduction is observed from the beginning of reaction and phenol and TOC conversion curves are close indicating that hydroxyl radicals are consumed from the beginning in the mineralization of by-products from phenol oxidation. These results suggest some differences in the reaction mechanism associated to the oxidation of the two compounds.

For alcohols, it is generally accepted the formation of a gold–alcoholate complex which evolves to more oxidized products, typically to the aldehyde, via β-hydrogen abstraction and without the participation of the oxidant, which eventually will regenerate the active site [47–49]. This mechanism cannot be assumed for phenols because of the absence of the β-hydrogen in the phenol molecule. Electrochemical analysis has been demonstrated covalent adsorption of phenol on gold electrodes by the oxygen atom and weak adsorption by the aromatic ring [50]. We believe that a similar situation can take place in the case of gold nanoparticles. To obtain experimental evidences on the different interaction between the two organic molecules tested and gold, adsorption experiments on gold supported on an inert support, reproducing the operating conditions of the oxidation tests but in absence of hydrogen peroxide were performed for each individual compound.

The results substantially showed higher uptake for benzyl alcohol than phenol (6.2 vs. 1.6 mmol per gram of Au/TiO_2, respectively, after 24 h contact time). Additionally, in the case of benzyl alcohol, benzaldehyde and benzoic acid were progressively detected upon time, remaining below 600 mg/L. These results confirm the reactivity between the alcohol and gold and also show the participation of water since benzoic acid instead of benzaldehyde was the major by-product [51]. In the case of phenol, experiment by-products were never detected in the liquid media and TOC and phenol disappearance were coincident so that only adsorption took place.

Therefore, benzyl alcohol and phenol show a different interaction with gold. We suggest that the kind of affinity of benzyl alcohol towards gold implies a major competition for the active sites that determines a slower decomposition of hydrogen peroxide. This leads to a progressive oxidation of benzyl alcohol and, as the concentration of the by-products increases, also a progressive mineralization (note that the benzyl alcohol by-products, benzaldehyde and benzoic acid, are more refractory to oxidation

than phenol and quinones). In the case of phenol-Au/TiO_2 systems, hydrogen peroxide is submitted to a lower competition for the active sites, which results in a faster hydrogen peroxide decomposition. Then, the radical species yield from this hydrogen peroxide decomposition are accumulated on the gold surface and recombined giving oxygen instead of reacting with phenol in solution. Therefore, the use of organic pollutants with reactivity towards gold, *i.e.* alcohols, results in somehow lower hydrogen peroxide decomposition rates and progressive oxidation and mineralization. It is a similar effect to the observed when a support with adsorption capacity towards the organic pollutant is employed.

3.3. Selectivity of the Au/C catalysts

Complete mineralization of phenol was far from being achieved with any of the gold catalysts tested (Fig. 3). These results are not unexpected attending to the nature of that compound and the mild operating conditions tested. Conversions of phenol were significantly higher than those of TOC, suggesting that relatively important amounts of by-products are produced. The by-products detected in the reaction media were aromatics and low molecular weight carboxylic acids, the latter were responsible of the decreasing pH of the reaction media up to around 2.3 after 24 h of reaction. The time-evolution of the reaction products and TOC removal with the Au(3)/C catalyst is depicted in Fig. 6, which also shows the results obtained with the bare activated carbon. The aromatic by-products identified in presence of gold were resorcinol, hydroquinone and *p*-benzoquinone (Fig. 6a) and the carboxylic acids were maleic, malonic, acetic, oxalic and formic, which have been grouped in Fig. 6b. According to the curve profiles (Fig. 6), the aromatic intermediates are completely converted upon sufficient reaction time to carboxylic acids, of substantially lower ecotoxicity and quite refractory to the oxidation under the conditions tested. Their residual concentration represented around 28% of the initial phenol in terms of carbon. The TOC values calculated from the identified by-products (not shown) were fairly close to the experimental TOC measurements (Fig. 6b) so that the oxidation intermediates are almost completely identified and quantified and condensation by-products, typically formed in Fenton and Fenton-like oxidations of phenol, are not present in the effluent.

The results of Fig. 6 also evidence the influence of gold on the by-product distribution. Resorcinol and hydroquinone were oxidized more rapidly than in the presence of bare carbon, appearing in lower concentrations, whereas catechol was not detected in presence of gold. A similar situation was observed with the different gold-sized-on-carbon catalysts prepared (Au(5)/C, Au(7)/C and Au(10)/C). Therefore, gold allows the hydroxylation of phenol in *meta* and *para* position (responsible for resorcinol and hydroquinone formation, respectively) and inhibits *orto*-hydroxylation (catechol formation). The different orientation of phenol on gold and on carbon surface may explain the different selectivity. Phenol is predominantly attached to gold by the oxygen atom [50] whereas the attachment on carbon occurs by the aromatic ring [52]. Thus, a vertical orientation to the surface and a parallel one are, respectively, expected. In the former, the attack of radicals to the *orto* position can be hindered and then catechol formation inhibited whereas in the latter the accessibility of the *orto* position is similar to the others. In addition to the faster oxidation of the aromatic intermediates, carboxylic acids were also detected in lower amounts than with bare carbon. Considering the refractoriness of the carboxylic acids and the enhanced TOC removal (Fig. 6b), the direct oxidation of phenol to CO_2 and H_2O is considered as a likely path.

The inhibition of the reaction path to catechol, ecotoxic intermediate typically formed in H_2O_2-oxidation of phenol, and the faster oxidation of dyhydroxybenzenes, oxidation hydroquinone being particularly important since it is by far the most ecotoxic intermediate of phenol oxidation route [53,54], together with the enhanced mineralization are important issues proving the beneficial effect of gold catalysts on the process investigated.

The distribution of by-products shown in Fig. 6 corresponds to a parallel–serial reaction network. Phenol is simultaneously oxidized to aromatic intermediates, carboxylic acids and CO_2 in parallel reactions. Subsequently, the aromatic by-products are oxidized to the organic acids of substantially lower ecotoxicity and higher biodegradability. Fig. 7 shows the proposed reaction pathway for the oxidation of phenol over supported gold on carbon nanoparticles.

4. Conclusions

Supported gold nanoparticles for wet peroxide oxidation processes must be designed considering that small particles, preferentially lower than 3 nm, exhibit higher TOF values and that the support can strongly enhance gold activity. The use of supports with high adsorption capacity such as activated carbons, and other modified carbonaceous materials, is preferred for a better use of the oxidant and to improve the TOF values for the oxidation and mineralization. The proposed mechanism for gold-on-carbon catalysts considers the preferential adsorption of the reactants on the gold-support interface, the production of hydroxyl and hydroperoxyl radicals on the gold surface and the reaction between hydroxyl radicals and phenol molecules on the gold surface as well as in the liquid phase. This process is more efficient for organic pollutants with a good affinity towards gold (those forming intermediate complexes *i.e.* alcohols). An important feature regarding the environmental interest of gold nanoparticles refers to catalytic selectivity with enhanced mineralization.

Acknowledgments

The authors thank the Spanish MICINN for the financial support through the projects CTQ2010-14807 and CTQ2008-03988/PPQ. The MINTEK Company is also gratefully acknowledged for the samples of Au/TiO_2 catalyst provided within the project "AuTEK Catalysis R&D".

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2011.09.020.

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Table S1. Binding energies (eV) of core electrons of Au $4f_{7/2}$ for supported gold nanoparticles. Peak percentages are given in parenthesis.

Sample	Au$4f_{7/2}$*	M2p/C1s	O/M
Au/TiO_2	83.9 (79) 85.8 (21)	458.5	-
Au/Fe_2O_3	84.0 (26) 84.9 (74)	710.7	-
Au(3)/C	84.0 (69) 85.4 (31)	284.6	0.09
Au(5)/C	83.9 (72) 85.6 (28)	284.6	0.14
Au(7)/C	84.0 (71) 85.5 (29)	284.6	0.05
Au(10)/C	84.0 (69) 85.6 (31)	284.6	0.10

*The shifts in the binding energy of electro-deficient gold species can be related to the different support and the synthesis method (Casaletto et al., Surf. Interface Anal. 38, (2006) 215; Ousmanea et al., Appl. Catal. B Environ., 101, (2011), 629).

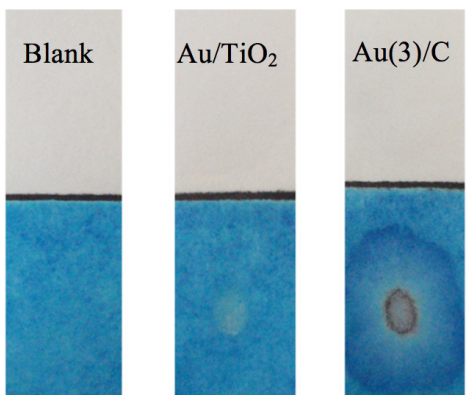
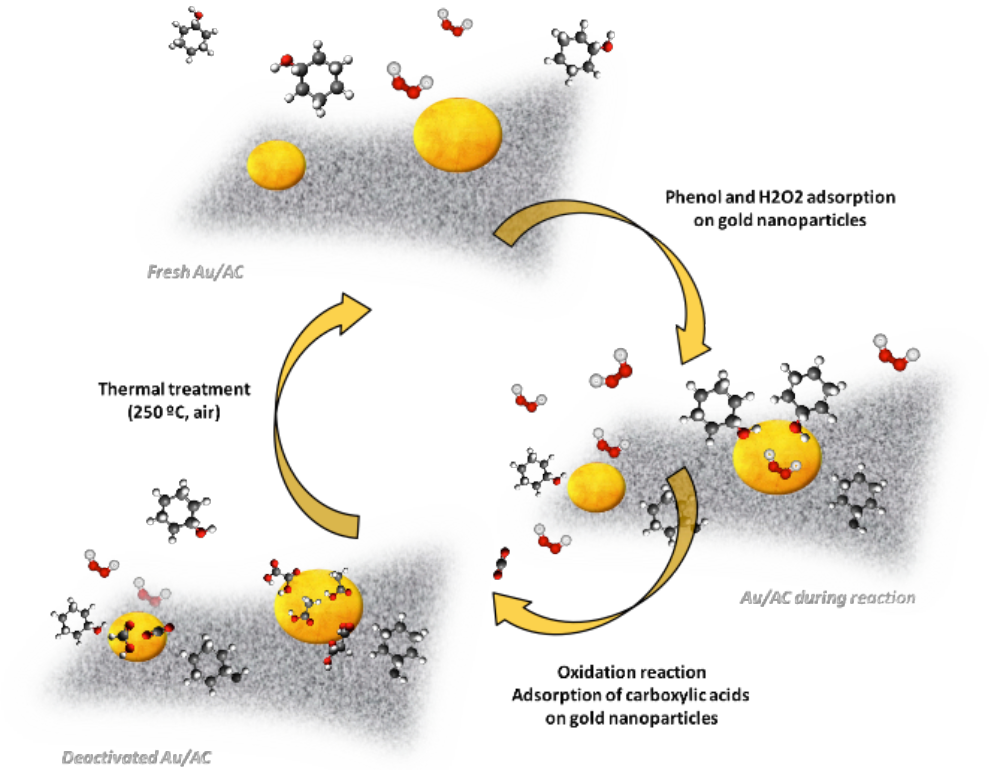


Figure S1. Strips of the methylene blue dye test from peroxidation experiments.

Capítulo II. Kinetics of wet peroxide oxidation of phenol over a gold/activated carbon catalyst



Kinetics of wet peroxide oxidation of phenol over a gold/activated carbon catalyst

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ARTICLE INFO

Keywords
gold nanoparticle,
phenol,
catalytic wet peroxide oxidation,
deactivation,
kinetic model.

ABSTRACT

Gold nanoparticles supported on activated carbon (Au/AC) are of promising interest in wet peroxide oxidation processes. In the present work, several experimental parameters, including initial pH (3.5-10.5), catalyst load (0-6 g/L), initial phenol concentration (0.1-5 g/L), hydrogen peroxide dosage (4-100% of the stoichiometric amount) and reaction temperature (50-80 ºC) have been studied in order to achieve an adequate degree of phenol abatement maintaining high efficiencies in hydrogen peroxide consumption. The results show that the use of Au/AC is only recommended for pollutant/carbon mass ratios of at least 0.4 and with hydrogen peroxide dosage corresponding to the stoichiometric amount. Effluents within a wide range of pH (3.5-7.5) can be treated. Gold catalyst is deactivated upon use but its activity can be completely restored by an oxidative thermal treatment at low temperature (200 ºC). According to the values of initial rates for hydrogen peroxide decomposition and phenol oxidation and considering their dependence on temperature, a kinetic model, based on power law equations, with partial orders of one and two for hydrogen peroxide and phenol, respectively, was successfully found from the reaction mechanism proposed. This model took into account catalyst deactivation with reaction time and it was able to simulate the experimental results obtained at different temperatures, initial phenol concentrations and hydrogen peroxide dosages.

Introduction

Catalytic wet peroxide oxidation (CWPO) is based on the oxidation of organic pollutants diluted in wastewater by hydroxyl and hydroperoxyl radicals produced by the catalytic decomposition of hydrogen peroxide under mild operating conditions (50-130 ºC, 1-5 atm) in the presence of a solid catalyst. This treatment arises with the aim of solving the main problems associated with the homogeneous process, namely Fenton oxidation (Fenton, 1894), in which dissolved iron salts are employed as catalyst. These drawbacks are the highly dependence on the pH solution, which must be within the 2.5-3.5 range (Neyens and Baeyens, 2003), the continuous loss of catalyst and the need to deal with the iron sludge generated during the reaction (Peratoner y Centi, 2005). In this sense, the use of solid catalysts by immobilization of the active phase over a convenient support offers an interesting solution. Most used catalysts in CWPO consist on iron supported on different materials, such as activated carbon (Zazo et al., 2006; Quintanilla et al., 2007; Rey et al., 2009), alumina (Munoz et al., 2013; Bautista et al., 2011; Inchaurrondo et al., 2012a), silica (Martínez et al., 2007; Melero et al., 2006; Melero et al., 2007; Melero et al., 2009), zeolites (Centi et al., 2000; Pestunova et al., 2002; Valkaj et al., 2011) or pillared clays (Barrault et al., 2000; Guo and Al-Dahhan, 2003; Catrinescu et al., 2003; Molina et al., 2006). The poor stability of the heterogeneous catalysts, caused by iron leaching (Zazo et al., 2006; Barrault et al., 2000; Perathoner and Centi, 2005, Garrido-Ramírez et al., 2010; Navalon et al, 2011; Rey et al, 2009) represents the main weakness of the process. The difficulty of developing suitable catalysts is noticed in the literature, and it remains as an important challenge for researchers.

The current trends in wastewater treatments explore the use of nanomaterials, being the most studied gold nanoparticles and carbon nanostructures, *viz.* nanotubes, nanofibers and xerogels (Quintanilla et al., 2012a). The recent researches carried out on the catalytic applications of gold nanoparticles indicate that CWPO is a fertile area for the application of this catalyst (Han et al., 2008, Navalon et al., 2010, Martin et al., 2011b, Quintanilla et al., 2012b) because of its appropriate good stability if the catalyst is adequately washed with aqueous base before reusing it in order to remove the dicarboxylic acids formed upon reaction that poison the gold surface (Martin et al, 2011a and b).

The activity of supported gold nanoparticles depends on many factors, *viz.* the preparation method (Martin et al., 2001a), the particle size (Martin et al., 2001a; Quintanilla et al., 2012b), the gold-support interaction and the nature of the support (Han et al., 2008, Navalon et al, 2010; Quintanilla et al., 2012b). The influence of the experimental conditions for the synthesis of gold supported on diamond nanoparticles (Au/npD) by deposition/precipitation methods was studied by Martin et at. (2010a). In this work, it was obtained that pH and the reduction treatment affected the gold particle size and consequently the catalyst activity of the nanoparticles in the CWPO of phenol. CWPO is clearly a gold size dependent reaction. The lower the particle size the lager surface area for supported gold nanoparticles and consequently the higher gold activity (Martin et al., 2001a; Quintanilla et al., 2012b). The nature of the support is also crucial for the activity of gold. The support can promote or even inhibit the activity of very

small gold nanoparticles (Quintanilla et al., 2012b). Up to now, gold nanoparticles deposited on hydroxyapatite (Au/HAP) (Han et al, 2008), diamond nanoparticle (Au/npD) (Martin et al., 2012b) or activated carbon (Au/AC) (Quintanilla et al 2012a) have exhibited adequate activity. However, these catalysts show a completely different efficiency of hydrogen peroxide consumption. Au/npD requires 6.5 times lower than the theoretical stoichiometric amount of hydrogen peroxide for complete phenol oxidation at 50 ºC, whereas Au/C employs the stoichiometric dosage at 80 ºC and Au/HAP, three times the stoichiometric amount at 70 ºC. Obviously, hydrogen peroxide decomposition also takes place on the support surface which can promote the consumption of radicals in parasitic reactions instead of reacting with organic molecules and consequently affecting the efficiency of the consumption of hydrogen peroxide.

Our previous studies based on the cost-effective catalyst Au/AC (Quintanilla et al., 2009 y 2012b), proposed a reaction mechanism and a reaction pathway for CWPO of phenol. In this work, the influence of experimental parameters, *viz.* initial pH, catalyst load, initial phenol concentration, hydrogen peroxide dosage and reaction temperature, and the catalyst stability and regeneration have been studied with the aim of developing a kinetic model that is able to describe the phenol oxidation and hydrogen peroxide decomposition rates on the basis of experiments carried out in the kinetic regime. Validation of the model will be done by fitting the experimental data obtained. To the best of our knowledge, no studies have been reported relating kinetic models of CWPO with gold catalysts.

2. Experimental

2.1. Catalyst

The 0.8 wt% Au/AC catalyst (Sample nº: 106C) was provided by Word Gold Council and applied as received. An overview of the physical and chemical properties of this catalyst is given in Table 1. The data are provided by the World Gold Council except for the specific surface area (S_{BET}), the external surface area (A_{ext}) and the content of elemental carbon and oxygen. The values of the first two properties were obtained from the N_2 adsorption/desorption isotherms at 77 K using a Micromeritics Tristar apparatus on the sample previously outgassed overnight at 150 ºC to a reduced pressure < 10^{-3} torr in order to ensure a dry clean surface. Elemental analyses were performed in a LECO Model CHNS-932 analyzer.

2.2. Oxidation experiments

The CWPO experiments were carried out batch-wise in a magnetically stirred three-necked glass reactor equipped with a reflux condenser. In a typical experiment, 45 mL of phenol solution at the desired pH (adjusted with HCl or NaOH) were placed in the reactor with the catalyst and heated up to the reaction temperature. After that, 5 mL of an adjusted concentration of hydrogen peroxide aqueous solution were added and the stirring at 1200 rpm started. Effluents at different reaction times were taken from the reactor and immediately analyzed. After 24 h of reaction, the heating was switched-off and the reactor cooled to room temperature in cold water. Then, the catalyst was separated by filtration (0.45 μm Nylon filter) and dried at 60 ºC. All the experiments were performed by duplicate being the standard deviation always less than 5%.

The oxidation runs were performed at different initial pH (3.5-10.5), phenol concentration (0.1-5 g/L) and temperatures (50-80 ºC). Also, catalyst loading ranged from 0 to 0.3 g and hydrogen concentration (4-100% of the stoichiometric amount for phenol mineralization) were tested. Before oxidation, the fresh catalyst was first washed with a phenol solution under the same experimental conditions as for the corresponding CWPO runs but in the absence of hydrogen peroxide in order to reduce the adsorption contribution to the phenol uptake.

2.3. Analytical methods

The progress of the reaction was followed by taking periodically liquid samples from the reactor. The liquid samples were analyzed by different procedures. Phenol and aromatic by-products were determined by high performance liquid chromatography, HPLC (Varian, mod. ProStar), low molecular weight acids by anionic suppression ionic chromatography, IC (Metrohm, mod. 761 Compact IC) and total organic carbon (TOC) using a TOC analyzer (O. I. Analytical, model 1010). Hydrogen peroxide concentration was determined by colorimetric titration with a UV 2100 Shimadzu UV-VIS spectrophotometer using the titanium sulfate method (Eisenberg, 1943). A more detailed description of these chemical analyses can be found elsewhere (Quintanilla et al., 2012b).

Table 1. Physico-chemical properties of Au/AC catalyst

Support		activated carbon
	Carbon type	Camel X40S
	Origin	vegetal
	Specific Surface Area, SBET (m2/g)	934
	External Area, Aext (m2/g)	56
	C (%)	76.6
	O (%)	20.6
Gold		
	Au content (%)	0.8
	dAu (nm)	10.5 ± 6.7
	Au0	75
	Au+	12.5
	Au3+	12.5

3. Results and discussion

3.1. Mass transfer considerations

The external mass transfer resistance from the liquid phase to the catalyst surface depends on the level of turbulence in the liquid phase. Hence, the effect of impeller rotation speed was investigated to identify the rate above which the apparent reaction rate does not change. The stirring rate tested values were 200 rpm (in an orbital shaker, Julabo, SW22) and 1200 and 1500 rpm (by a magnetic stirring), while the other reaction conditions were maintained invariable (pH_0=3.5, C_{cat}=2.5 g/L, $C_{Ph,0}$=5 g/L, $C_{H2O2,0}$=25 g/L, T=80 ºC). In all the studied range, the profiles of phenol and hydrogen peroxide conversions obtained upon reaction time were independent of the rotation speed (see Figure S1 of Supporting Information) confirming that the system is not controlled by the liquid-solid mass transport. The impeller speed was set at 1200 rpm for further experiments. The Weisz-Prater criterion has been used to test whether slow internal diffusion was limiting the reaction:

$$\Phi = \eta \cdot \phi^2 = \left(\frac{observed\_rate}{diffusion\_rate} \right) = \left(\frac{r_{obs} \cdot L_s^{\,2}}{D_{eff} \cdot c_s} \right) \cdot \left(\frac{n+1}{2} \right) < 0.15$$

[1]

Assuming pseudo-first order kinetics (n=1), the above expression is simplified as follows:

$$\Phi = \eta \cdot \phi^2 = \left(\frac{K_{obs} \cdot L_s^{\,2}}{D_{eff}} \right) < 0.15$$

[2]

The observed kinetic rate constant for phenol oxidation (K_{obs}=7.30·10^{-5} L/g_{cat}·s) was calculated using a power-law pseudo-first order model at the highest temperature (80 ºC) and catalyst load (2.5 g/L). L_s is defined as a characteristic length of the catalyst particle ($d_p/6$ = 1.33·10^{-5} m). The value of effective diffusivity (D_{eff}) of phenol in activated carbons is around 1.1·10^{-9} m^2/s (Bhatia et al., 1990). By substituting these values in Eq. [2], the Wheeler-Weisz modulus results 6.3·10^{-5}, therefore internal diffusion limitation can be excluded.

3.2. Influence of reaction conditions

The efficient consumption of hydrogen peroxide is of main concern in CWPO processes (Botas et al., 2010; Zazo et al., 2011; Martin et al., 2011b; Inchaurrondo et al., 2012b; Domínguez et al., 2013). By operating at adequate conditions, the parasitic reactions consuming ·OH and ·OOH radicals to produce oxygen, a non-effective specie under the operating range commonly used in CWPO, can be reduced on the catalyst surface, in particular when using activated carbons (Domínguez et al., 2013). In order to find those conditions for Au/AC catalysts, a study of the influence of reaction conditions has been carried out.

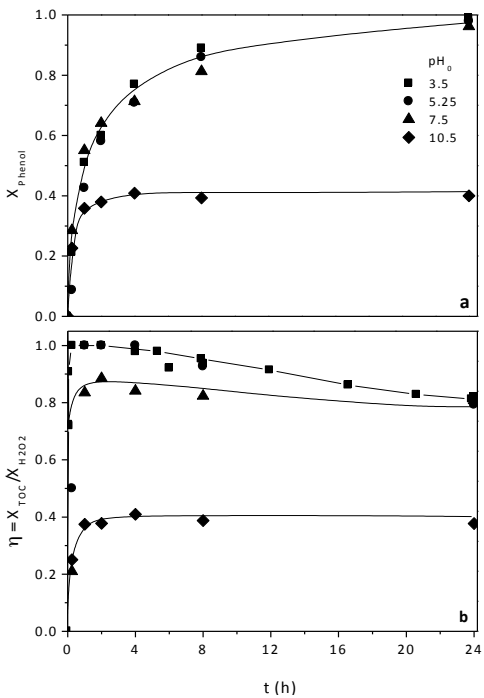

Figure 1. Effect of initial pH on phenol disappearance (a) and hydrogen peroxide efficiency (b). Operating conditions, Ccat=2.5 g/L, CPh,0=5 g/L, CH2O2,0=25 g/L, T=80 ºC.

3.2.1. Initial pH

It is well known that wet peroxide oxidation is sensitive to the pH and usually acid conditions are required (Neyens and Baeyens, 2003). However, the use of solid catalysts widens the interval of work and neutral pH has been also reported (Perathoner and Centi, 2005). In the presence of Au/AC catalyst, this variable was explored within the range from 3.5 to 10.5. The starting pH value was adjusted (but not buffered) with 1M solution of HCl or NaOH, as corresponded. The temporal profiles of phenol conversion and hydrogen peroxide efficiency (η), the later defined as the amount of TOC removed per hydrogen peroxide consumed, are depicted in Figure 1a and b, respectively. As can be seen, when the initial pH is acid or neutral, phenol conversion is not affected by this variable and similar phenol conversion profiles are obtained at values of pH from 3.5 to 7.5, achieving complete phenol depletion after 24 h of reaction. However, different consumption of hydrogen peroxide is observed. At acid pH, equal to 3.5 or 5.25,

the initial efficiency in the consumption of hydrogen peroxide is maximum (η≈1) and slightly decreases upon reaction time with the consumption of the organic matter up to values of 0.8, while at neutral pH, a value equal to 7.5, the initial efficiency is somehow diminished (η≈0.88) and reduced to the same value of 0.8 during the 24 h reaction. On the other hand, at basic pH (10.5), phenol conversion achieves an asymptotic value, at around a values of 40%, from the early stages of the reaction due to the rapid consumption of hydrogen peroxide (X_{H2O2}=99% in 1 h reaction). Besides, very low efficiencies of hydrogen peroxide are obtained (η<0.4) (Figure 1b) due to its favored decomposition into oxygen and water through parasitic reactions in base solutions.

According to these results, effluents with a wide range of pH (3.5-7-5) can be treated with Au/AC catalyst though acidic conditions assure a more efficient consumption of hydrogen peroxide.

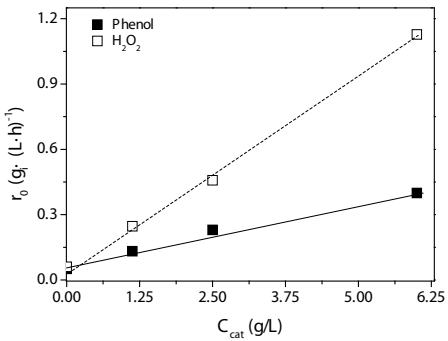

Figure 2. Effect of catalyst loading on phenol oxidation and hydrogen peroxide decomposition. Operating conditions: CPh,0=1 g/L, CH2O2,0=5 g/L, T=80 ºC, pH0=3.5.

3.2.2. Catalyst loading

The effect of catalyst loading was investigated at 80 ºC and initial phenol concentration of 1 g/L Figure 2 shows the dependence of the initial reaction rates of phenol and hydrogen peroxide disappearance on the catalyst load. Increasing the catalyst concentration in the range 0-6 g/L, the initial reaction rates increase linearly. Besides, homogeneous reaction in the absence of catalyst can be discarded. In this case, conversions of 5 and 9% were obtained for hydrogen peroxide and phenol degradation at 4 h reaction time, respectively, which are negligible comparing to those obtained in the presence of catalyst, X_{Ph}=55, X_{H2O2}=69% at C_{cat}=2.5 g/L.

3.2.3. Phenol concentration

The effect of the initial concentration of phenol was investigated in the range of 0.1-5 g/L at 80 °C in the presence of Au/AC catalyst. Figure 3a shows the phenol conversion with time at five different initial phenol concentrations. As seen, the higher initial phenol concentration, the higher conversions under otherwise identical conditions. The explanation for these results can be found in the efficiency values for hydrogen peroxide consumption, displayed in Figure 3b. Only at phenol concentrations as high as 5g/L, efficiency values are equal to one and as the initial concentration decreases so does the initial hydrogen peroxide efficiency, achieving null values for phenol concentrations of 0.1 g/L. These findings are consistent with the results reported by (Domínguez et al., 2013) dealing with activated carbons as catalysts for CWPO of phenol. As in that case, working at high pollutant/carbon mass ratios, there is a high occupancy of the surface active sites or reduction of those available for hydrogen peroxide decomposition, and it is possible to avoid or significantly reduce the non-effective consumption of hydrogen peroxide in parasitic reactions thus giving rise to improved efficiency. According to these results (Figure 3a and b), the use of Au/AC in CWPO is recommended for pollutant/carbon mass ratios of at least 0.4 when the stoichiometric amount of hydrogen peroxide is used. On the other hand, the initial reaction rate within this inlet concentration range, given in Figure 4, shows that the order of reaction with respect to phenol is 2.

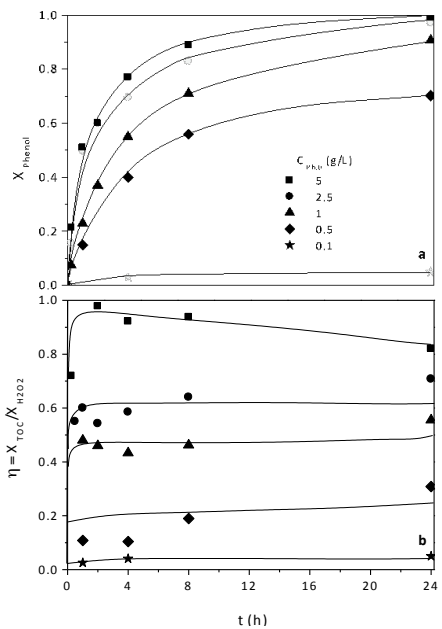

Figure 3. Effect of the initial phenol concentration on phenol disappearance (a) and hydrogen peroxide efficiency (b). Operating conditions: CPh,0=0.1-5 g/L, CH2O2,0=stoichiometric dosage, Ccat=2.5 g/L, T=80 ºC, pH0=3.5.

3.2.4 Hydrogen peroxide concentration

Different initial hydrogen peroxide dosages were tested viz. 1, 12.5 and 25 g/L, in order to oxidize 5 g/L of phenol at 50 ºC. These values correspond to 4, 50 and 100% of the stoichiometric amount of hydrogen peroxide for complete phenol oxidation to CO2 and water. Phenol conversion vs. reaction time is depicted in Figure 5, showing an important hydrogen peroxide dependency. On the other hand, the initial reaction rate of hydrogen peroxide decomposition increases linearly with an increase in the inlet hydrogen peroxide concentration (Figure 4), and a reaction order of 1 with respect to hydrogen peroxide was obtained.

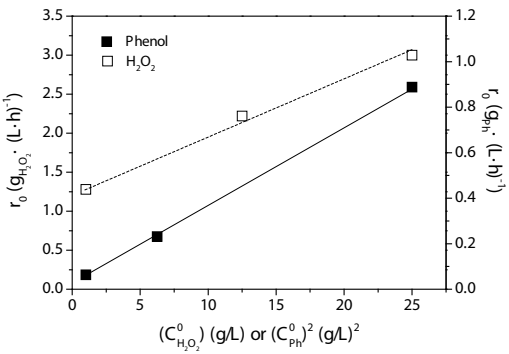

Figure 4. Lineal relationship between H2O2 and phenol initial rates with initial CH2O2 and CPh2 , respectively. Operating conditions: T=50 ºC, Ccat=2.5 g/L, pH0=3.5.

3.2.5 Temperature dependency

Figure 6 presents the phenol conversion profiles under different temperatures, 50, 65 and 80 °C at 5 g/L of initial phenol concentration and the corresponding stoichiometric amount of hydrogen peroxide. Total elimination of phenol was achieved at 80 °C after 24 h reaction, while the maximum phenol conversion obtained at 50 ºC was about 45%. As expected, higher phenol removal rates were observed at higher temperatures. The observed activation energy for the abatement of phenol has been determined from the Arrhenius plot shown in Figure 7, in which the logarithm of the apparent kinetic constant kapp, calculated from Eq. [3], against the reciprocal of the temperature has been plotted, being this value 74,200±2,600 J/mol.

$$(-ro) = k_{app} \cdot C_{Ph}^{z} \cdot C_{H2O2}^{1}$$

[3]

3.3. Phenol mineralization

Total organic carbon concentration upon reaction time was followed in all cases. Conversions of phenol were always significantly higher than those of TOC, suggesting that relatively important amounts of by-products were produced during reaction. As an example, the temporal profiles of TOC concentration at 80 ºC and 5 g/L of initial concentration is shown in Figure 8. The by-products detected in the reaction media were aromatics compounds (mainly resorcinol, hydroquinone and p-benzoquinone) and low molecular weight carboxylic acids (maleic, malonic, oxalic, acetic and formic acids).

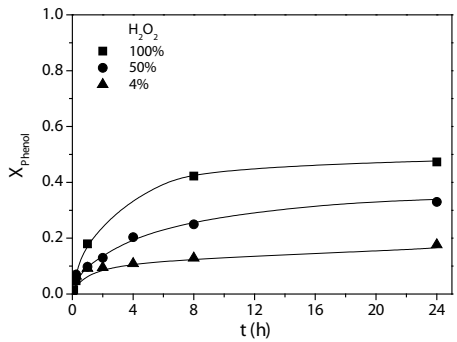

Figure 5. Effect of hydrogen peroxide dosage on phenol disappearance. Operating conditions. Ccat= 2.5 g/L, CPh,0=5 g/L, T=50 ºC, pH0=3.5.

The TOC values calculated from these identified by-products were close to the experimental TOC measurements, differences lower than 10 % were found after 24 h reaction (Figure 8), indicating that the presence of important condensation by-products in the liquid effluents, typically detected in Fenton oxidation Zazo et al. (2005), can be considered negligible in the presence of Au/AC catalyst.

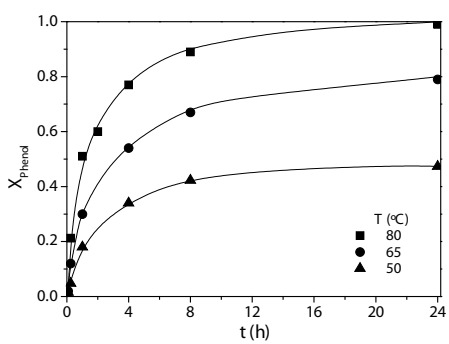

Figure 6. Temperature effect on phenol disappearance. Operating conditions: Ccat= 2.5 g/L, CPh,0=5 g/L, CH2O2,0=25 g/L, pH0=3.5.

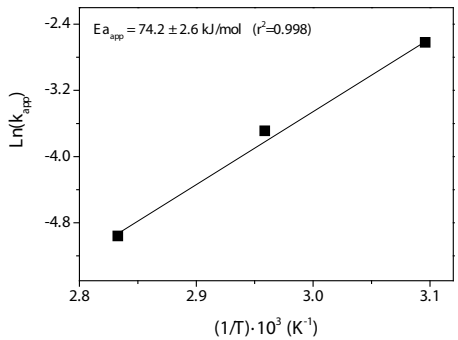

Figure 7. Arrhenius plot of CWPO with Au/AC at the operating conditions of Figure 6.

3.4. Catalyst stability and regenerability

Au/AC was tested in four successive runs in order to analyze its stability. In each cycle, the catalyst was used during 24 h in reaction, then separated by filtration and dried at 60 ºC for 24 h without any further treatment. The stability experiments were carried out by contacting the aged catalyst with fresh phenol and hydrogen peroxide solutions. The apparent kinetic constant values ($k_{app,}$ L^2/g_{Ph} g_{H2O2}·h) for each reaction were calculated from the observed initial reaction rates considering the reaction orders previously obtained in Eq. [3].

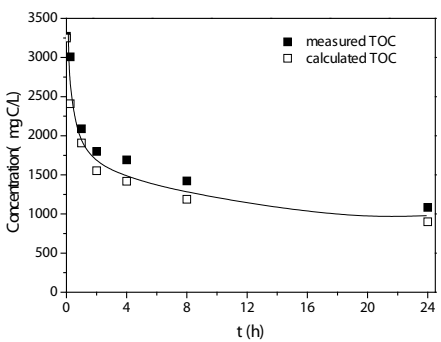

Figure 8. Time-evolution of measured and calculated TOC values upon CWPO of phenol with Au/AC. Operating conditions, Ccat=2.5 g/L, CPh,0=5 g/L, CH2O2,0=25 g/L, T=80 ºC, pH0=3.5.

Figure 9 shows these values for each catalytic cycle, and also the one obtained in presence of the bare activated carbon, which was included for the sake of comparison. Clearly, gold catalyst is deactivated after its first use and the activity exhibited from the second cycle can be mainly attributed to the carbon support. In order to get an insight into the causes of this rapid deactivation, some reactor effluents were analyzed and the 1st used catalyst characterized and submitted at different treatments to reestablish the activity.

No traces of gold were detected in the liquid samples by TXRF, therefore, deactivation by gold leaching was discarded. On the other hand, it is well-known that carboxylate species (Nijhuis et al., 2005; Abad et al., 2008; Martin et al. 2011a and 2011b) strongly adsorb on gold nanoparticle surface which ultimately lead to catalyst poisoning. In particular for CWPO process, dicarboxylic acids, which are the typical oxidation by-products, have been considered the responsible of the gold deactivation (Martin et al., 2011a and 2011b). At the operating conditions of Figure 9, as much as 900 mg C/L of low-weight carboxylic acids were measured after 24 h reaction time being maleic (184 mg C/L), malonic (239 mg C/L), oxalic (49 mg C/L), acetic (332 mg C/L) and formic (70 mg C/L) the main dicarboxylic acids present.

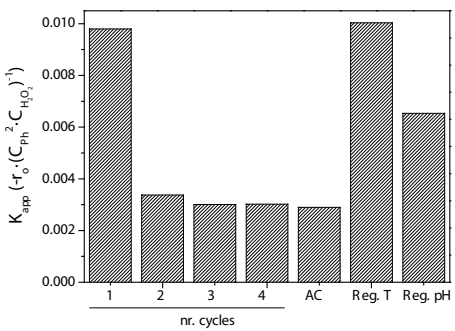

Figure 9. Evolution of kapp with different catalyst cycles and after regeneration treatments for Au/C catalyst. Operating conditions, Ccat=2.5 g/L, CPh,0=5 g/L, CH2O2,0=25 g/L, T=80 ºC, pH0=3.5.

Strong basic washings of the spent catalyst are effective to dissolve these species and to get rid of this type of poison (Martin et al., 2011a, Abad, et al., 2008). Hence, the recovery of the gold activity was first carried out by washing the used Au/AC catalyst at room conditions in basic media (Na_2CO_3, pH=14, C_{cat}=2g/L, t= 3h) and then washing it with distilled water until neutral pH. During this treatment, 2 wt% of the initial gold loaded in the catalyst was leached and the catalyst activity recovered in a 60% (Figure 9). Alternatively, spent catalyst was submitted to an oxidative thermal treatment at the low temperature of 200 ºC during 14 h in air atmosphere in order to burn-off the adsorbed species. This treatment resulted in a 10% mass loss of catalyst (the difference in weight before and after the heat treatment) and the catalyst activity was completely restored (Figure 9).

3.5. Kinetics

3.5.1. Model

A reaction mechanism for the oxidation of phenol on the carbon-supported gold nanoparticles was proposed in a previous work (Quintanilla et al., 2012). It was found that CWPO of phenol over Au/AC catalyst proceeds through a complex scheme of reactions involving many intermediates species, and it was postulated, in a simple way and according to the experimental findings, by the following steps: (i) adsorption of phenol and, preferentially, hydrogen peroxide on the gold-support interface, (ii) production of hydroxyl and hydroperoxyl radicals on the gold surface though some extension also occurs on the carbon surface and (iii) reactions between hydroxyl and phenol molecules on the gold surface. Also, hydroxyl radicals are released to the liquid phase where they react with phenol in solution. Parasite reactions, by the recombination of radicals species present, can take place yielding hydrogen peroxide and also oxygen and water.
According to the above mechanism, and considering only the main reactions for CWPO of phenol, the following reaction scheme has been taking into account in this study:
Hydrogen peroxide decomposition into hydroxyl and hydroperoxyl radicals in the presence of gold nanoparticles by a redox cycle:

$$H_2O_2 + Au^0 \rightarrow \cdot OH + OH^- + Au^+ \quad [4]$$

$$H_2O_2 + Au^+ \rightarrow \cdot OOH + H^+ + Au^0 \quad [5]$$

According to the analyses of the initial rates for hydrogen peroxide decomposition (Figures 2 and 4), this mechanism can be described by a power law equation, in which the partial order for catalyst and hydrogen peroxide is equal to one:

$$r_{H2O2} = k_{H2O2} \cdot C_{cat} \cdot C_{H2O2} \quad [6]$$

k_{H2O2} ($L/g_{cat}\cdot h$) being the kinetic rate constant for hydrogen peroxide decomposition.
Phenol oxidation by radical species into aromatic compounds, low-molecular carboxylic acids, carbon dioxide and water:

$$Phenol + \cdot OH + \cdot OOH \rightarrow Aromatics + Acids + CO_2 + HO_2 \quad [7]$$

Figure 2 showed the linear dependence of the phenol reaction rate on the catalyst load and Figure 4, a partial order equal to two with respect to initial phenol concentration. Therefore, phenol disappearance can be described as follows:

$$r_{Ph} = k_{Ph} \cdot C_{cat} \cdot C_{\cdot OH+\cdot OOH} \cdot C_{Ph}^2 \quad [8]$$

k_{Ph} ($L^3/ g_{cat}\cdot g_{(\cdot OH+\cdot OOH)}\cdot g_{Ph}\cdot h$) being the kinetic rate constant for phenol oxidation.

Considering a steady state for radical species, their concentration is constant and included in the kinetic constant, resulting:

$$r_{Ph} = k_{Ph'} \cdot C_{cat} \cdot C_{Ph}^2 \quad [9]$$

Where $k_{Ph'}$ ($L^2/g_{cat}\cdot g_{Ph}\cdot h$) is the modified kinetic rate constant for phenol oxidation including the concentration of radical species.
The kinetic model must take deactivation process into account (Figure 9). As previously mentioned, Au/AC catalyst is deactivated upon reaction time due to gold poisoning by low-weight carboxylic acid by-products. Then, the catalyst concentration can be described as a decreasing-time function:

$$C_{cat} = k_{cat} \cdot e^{-K_d \cdot t} \quad [10]$$

being k_{cat} (g_{cat}/L) and k_d (h^{-1}) the kinetic rate constants for the catalyst and the catalyst deactivation, respectively.
Substituting this temporal function, Eq. [10], in Eqs. [6] and [9] and grouping terms, the following model based on power law expression assuming that the surface reaction is rate-determining was found to merit consideration:

$$r_{H2O2} = k'_{H2O2} \cdot e^{-k_{d,H2O2}\cdot t} \cdot C_{H2O2} \quad [11]$$

$$r_{Ph} = k'_{Ph'} \cdot e^{-k_{d,Ph}\cdot t} \cdot C_{Ph}^2 \quad [12]$$

where the kinetic constants for hydrogen peroxide decomposition k'_{H2O2} (h-1) and phenol oxidation $k'_{Ph'}$ (L/gPh·h) are defined according to the Arrhenius law.
3.5.2. Modeling: parameter estimation
Since the reactor can be assumed to be perfectly stirred (Figure S1), the batch-reactor model was used:

$$-\frac{dC_{H2O2}}{dt} = r_{H2O2} \quad [13]$$

$$-\frac{dC_{Ph}}{dt} = r_{Ph} \quad [14]$$

with initial condition: t=0 CPh= CPh,0
CH2O2= CH2O2,0
The numerical integration of the differential equations and parameter estimation have been carried out with the software package Scientist 3.0 (nonlinear optimization). The predicted model found is:

$$r_{H2O2}\left(\frac{g_{H2O2}}{L\cdot h}\right) = [5{,}447 \pm 2.58\ (h^{-1})] \cdot e^{\frac{-30{,}330\pm 2{,}660\left(\frac{J}{mol}\right)}{R\cdot T}} \cdot e^{-k_{d,H2O2}(h^{-1})\cdot t(h)} \cdot C_{H2O2}\left(\frac{g_{PH2O2}}{L}\right) \quad [15]$$

$$r_{Ph}\left(\frac{g_{Ph}}{L\cdot h}\right) = 61{,}635 \pm 34\left(\frac{L}{g_{Ph}\cdot h}\right) \cdot e^{\frac{-45{,}781\pm 9{,}145\left(\frac{J}{mol}\right)}{R\cdot T}} \cdot e^{-k_{d,Ph}(h^{-1})\cdot t(h)} \cdot C_{Ph}^2\left(\frac{g_{Ph}}{L}\right)^2 \quad [16]$$

The kinetic parameter values for the deactivation constant corresponding to hydrogen peroxide and phenol at the differ-

ent temperature tested are collected in Table 2. As expected, phenol oxidation is the rate determining step as indicated by the higher activation energy value. The results of the model predictions along with the experimental data are shown in Figures 10 and 11, for hydrogen peroxide consumption and phenol disappearance, respectively. The validation of the model can be better proven by the parity plot of hydrogen peroxide and phenol concentrations in Figure 12. No trend exists between the experimental observations and the results calculated from Eq. [15] and [16]. Thus, good fits of the reactants were achieved with the proposed kinetic model.

Table 2. Deactivation kinetic constants (h-1) estimated at different temperatures for the proposed model

Parameter	Value
$k_{d,H2O2,80ºC}$	0.0903±0.0068
$k_{d,H2O2,65ºC}$	0.1326±0.0097
$k_{d,H2O2,50ºC}$	0.3060±0.0420
$k_{d,Ph,80ºC}$	0.0555±0.0071
$k_{d,Ph,65ºC}$	0.1663±0.0531
$k_{d,Ph,50ºC}$	0.2567±0.0877

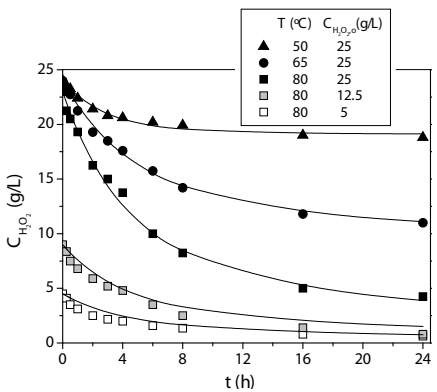

Figure 10. Experimental data (symbols) and predicted values (curves) of H2O2 concentration at the different conditions tested.

4. Conclusions

The effect of several experimental parameters, *viz.* pH, catalyst load, initial phenol concentration, hydrogen peroxide dosage and temperature, influencing the efficiency of hydrogen peroxide consumption in CWPO of phenol over Au/AC, has been studied. In order to achieve an efficient consumption of this reagent, operating at pollutant/carbon mass ratios ≥ 0.4 is needed. In this way, the active sites for hydrogen peroxide decomposition are highly covered by phenol molecules and the extension of parasitic reactions, consuming radical species, is minimized. Phenol solutions with acid or neutral pH can be treated in the presence of Au/AC, widening the pH range commonly used in CWPO processes. Both, catalyst load and reaction temperature increase the reaction rates of hydrogen peroxide and therefore, of phenol oxidation.

Calculated and experimental TOC values in the presence of Au/AC catalyst were fairly close, suggesting that condensation by-products in the liquid phase, typically formed in Fenton oxidation, are not important.

Au/AC showed high resistance against leaching but was deactivated upon use due to the adsorption of dicarboxylic acids on gold nanoparticles. However, the activity can be easily recovered by a thermal treatment at low temperature in air atmosphere (200 ºC, 14 h).

A kinetic model based on a simplified reaction mechanism that considers partial orders of one and two for hydrogen peroxide and phenol, respectively, and takes into account the catalyst deactivation with reaction time has been found to properly predict the hydrogen peroxide and phenol experimental concentrations in a wide range of temperatures (50-80 ºC) and initial phenol concentrations (1-5 g/L).

Acknowledgments

The authors wish to thank the Spanish MICINN for the financial support through the projects CTQ2008-03988/PPQ and CTQ2010-14807. The Comunidad Autónoma de Madrid is also gratefully acknowledged for the financial support through the project S2009/AMB-1588.

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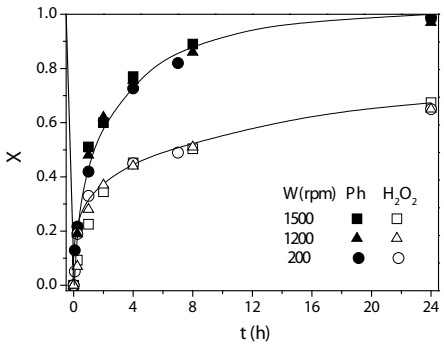
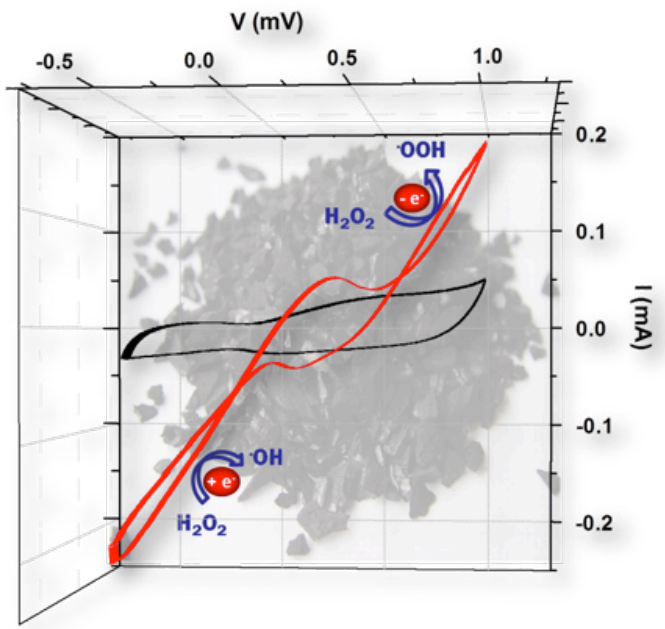


Figure S1. Effect of the stirring rate on phenol and hydrogen peroxide conversion. Operating conditions: pH0=3.5, Ccat=2.5 g/L, CPh,0=5 g/L, CH2O2,0=25 g/L, T=80 ºC.

Bloque II

Catalizadores basados en materiales carbonosos para procesos de oxidación húmeda con peróxido de hidrógeno

Capítulo III. The use of cyclic voltammetry to asses the activity of carbon materials for hydrogen peroxide decomposition



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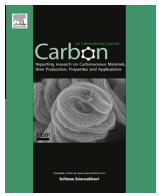

The use of cyclic voltammetry to assess the activity of carbon materials for hydrogen peroxide decomposition

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ARTICLE INFO

Article history:
Received 10 January 2013
Accepted 27 March 2013
Available online 6 April 2013

ABSTRACT

It is known that carbon materials catalyze hydrogen peroxide decomposition in aqueous media. However, the catalytic activity of a particular carbon is dependent on various coupled structural, textural and chemical characteristics of the material, such that, formerly, the prediction of activity has not been possible. Here, the application of cyclic voltammetry (CV) is introduced as a rapid and conclusive technique in this respect. Three classes of carbon materials have been investigated: activated carbons, carbon blacks, and graphites, including some selected acid-washed samples which were used to examine the roles of mineral matter and surface oxygen. Characterization by electrochemical capacity measurements with CV, together with catalytic activity tests for hydrogen peroxide decomposition, reveal that the exchange current is directly proportional to the catalytic activity for hydrogen peroxide decomposition. That is, a linear dependence was found between this variable and the apparent first order catalytic decomposition rate constant. CV measurements with modified carbons also allow the elucidation of the effects of physicochemical characteristics of carbon materials on the rate of hydrogen peroxide decomposition.

1. Introduction

Hydrogen peroxide decomposition over carbon materials is of interest in the field of wastewater treatment because it leads to the formation of radicals (·OH and ·OOH), highly oxidizing species allowing the breakdown of organic pollutants in aqueous solution and/or adsorbed onto the carbon surface [1]. That decomposition reaction can take place due to the donor–acceptor properties of the carbon surface (C), through an electron-transfer mechanism similar to the Fenton reaction (Fig. 1), acting C and C^+ as the reduced (1) and oxidized (2) carbon states, respectively [2–7].

This redox cycle is highly dependent on the structural, textural and chemical characteristics of carbon materials [7,8]. The most important features affecting the electron-transfer reactivity and, consequently, the carbon activity are the ash content [9–13], the microstructure and porosity [3,7,8] and chemical composition, specifically the quantity and nature of surface functional groups [1,4–10,12,14]. For this reason, the studies dealing with the application of carbon catalysts in hydrogen peroxide decomposition, or the processes in which this reaction is involved viz. wastewater treatments by wet peroxide oxidation [6,7,10,12,15], usually include a number of tedious, time-consuming and expensive characterization techniques (e.g., Raman spectra, Fourier transform infrared spectroscopy (FTIR), diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), thermal gravimetric analysis (TGA), elemental analysis (EA), X-ray diffraction (XRD), total reflection X-ray fluorescence (TXRF), induced coupled plasma (ICP), N_2 adsorption/desorption isotherms). In spite of this, achieving conclusive

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0008-6223/$ - see front matter
http://dx.doi.org/10.1016/j.carbon.2013.03.058

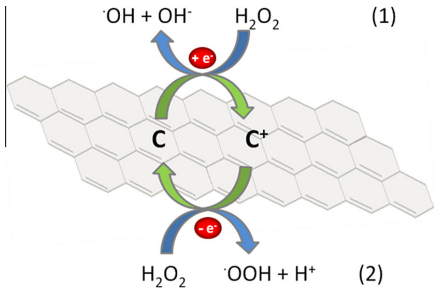

Fig. 1 – Hydrogen peroxide reduction (1) and oxidation (2) over carbon materials.

results about the characteristics of carbon materials, directly or indirectly related to the activity, is not always possible. The reason for this is that the different issues cannot be analyzed independently, due to the difficulty of tailoring a single carbon characteristic upon the preparation process, without affecting the rest. Therefore, the occurrence of coupled effects is common and makes impracticable a reasonable prediction of the catalytic activity of carbon materials as a function of their structural and physico-chemical characteristics.

In this paper, we present cyclic voltammetry as a simple and direct technique which is able to provide conclusive information about the catalytic activity of carbon materials in hydrogen peroxide decomposition reaction. We demonstrate by using different types of carbon materials viz. activated carbons, carbon blacks and graphites, that the electrochemical behaviour of the carbon for some particular structural and physico-chemical characteristics given, governs the activity. This technique has occasionally been used to characterize metallic catalysts [16] and to predict their activity [17,18] but to the best of our knowledge it has not yet been reported for carbon materials.

2. Experimental

2.1. Carbon materials

Three types of commercial carbon materials with different structural, textural and chemical characteristics have been studied: two activated carbons (AC), supplied by Merck (AC-M, Ref.: 102514) and Panreac (AC-P, Ref.: 3108L); two carbon blacks (CB), supplied by Chemviron (CB-C, Ref.: 2156090) and Vulcan (CB-V, Ref.: CC72R) and two graphites (G), supplied by Sigma–Aldrich (G-S, Ref.: 282863) and Fluka (G-F, Ref.: 1249167). All samples were provided in powder form except for the AC-M, which was sieved to 80–100 μm before use.

In addition, the AC-M and G-S samples were treated with concentrated HCl (37%) solution, at room temperature for 4 h (2 g sample/25 mL HCl solution), and then washed with distilled water until constant pH, filtered, and dried overnight at 60 °C. The resulting carbons were identified as AC-M-HCl and G-S-HCl, respectively. A similar treatment was performed on AC-P but using HNO_3 (65%) yielding the AC-P-HNO_3 sample. Table 1 summarizes the nomenclature of all the carbon materials tested.

2.2. Characterization

The structural parameters were determined by X-ray diffraction. XRD patterns were obtained using a Siemens Model D5000 X-ray diffractometer, Cu Kα (8.04 keV) radiation, and a step of 0.02°/s for 2θ=5–100°. XRD data were analyzed with PDF 2000 (JCPDS-ICDD) software.

The BET surface area (S_{BET}) of the initial and modified carbons was obtained from the 77 K N_2 adsorption/desorption isotherms using Micromeritics Tristar apparatus, outgassing the samples overnight at 150 °C to a residual pressure of $<10^{-3}$ torr. The external or non-microporous surface area (A_{ext}) was calculated by the *t*-method.

Elemental analyses of the carbon materials were performed in a LECO Model CHNS-932 apparatus. The identification and quantification of the elements was determined by TXRF (Extra-II Rich & Seifert spectrometer).

The surface oxygen groups were analyzed by temperature-programmed desorption under N_2 (TPD). A 100 mg sample of carbon was placed in a quartz tube and heated at 10 °C/min from room temperature up to 900 °C under a continuous N_2 flow of 1 L/min. The CO_2 and CO evolved were measured in a gas analyzer (SIEMENS mod. Utramat 22).

2.3. Cyclic voltammetry experiments

Electrochemical measurements were carried out in a conventional three-electrode electrochemical cell, using a

Table 1 – Structural, textural and chemical characteristics of the carbon materials tested.

Sample	d_{002} (Å)	L_c (Å)	L_a (Å)	S_{BET} (m^2/g)	A_{ext} (m^2/g)	Ashes (%)	Fe (%)	CO_2 (μmol/g)	CO (μmol/g)
AC-M	3.614	17.7	38.0	1019	175	4.00	0.04	30	320
AC-M-HCl	–	–	–	843	128	1.38	0.03	74	562
AC-P	3.793	16.2	36.0	931	472	1.00	0.01	140	662
AC-P-HNO_3	–	–	–	894	354	0.35	0.01	669	1866
CB-C	3.476	70.8	65.7	75	75	0.00	0.00	83	160
CB-V	3.618	38.7	38.9	233	110	1.00	0.00	148	106
G-S	3.383	440.9	487.0	12	12	0.50	0.44	105	36
G-S-HCl	–	–	–	11	11	0.08	0.02	–	–
G-F	3.367	466.3	488.7	7	5	0.20	0.00	128	79

computerized potentiostat (Autolab PGSTAT 302, Eco Chemie) controlled by GPES software. A glassy carbon rotating disk electrode (3 mm diameter) was used as substrate for the carbon samples (working electrode). Prior to each test, the electrode was polished to 3 μm with alumina powder and rinsed with Milli-Q ultrapure water. A gold electrode was used as the counter electrode and a saturated Ag/AgCl, KCl electrode served as the reference. The electrochemical experiments were carried out at room temperature and ambient pressure using an HCl (pH = 3.5) solution as the electrolyte.

The carbons under study were deposited on the working electrode as an ink. Typically, 6 mg of sample was dispersed in Milli-Q water (730 μL) with ultrasonic agitation (Hyelscher, UP50H), to obtain a homogeneous suspension; 10 μL of this suspension was carefully dropped on a glassy carbon electrode and allowed to dry at room temperature for 60 min to obtain a uniform film.

In a typical experiment, the working electrode was subjected to cyclic voltammetry (CV) measurements in a background solution (HCl, pH = 3.5) at a sweep rate (v) of 100 mV/s and the potential range from − 0.6 to 1.0 V. Once unchanging cyclic voltammograms were obtained for several cycles (variations in the coulumbic charge lower than 2%), the sweep rate was reduced to a value of 10 mV/s, and data acquisition started. First, the coulombic charge (CC) for the carbon was calculated from the background voltammogram. Then, the precise volume of hydrogen peroxide (30%) was added to the electrolyte solution and the open circuit potential (E_{ocp}) registered. Finally, a new CV was recorded to determine the electrochemical behavior of the carbon materials in the presence of hydrogen peroxide. The absence of diffusion limitations in the interphase for the overall electrochemical process should be noted because identical results were obtained within the rotation velocity range from 0 to 3000 rpm, as was expected for a surface-controlled process. All measurements were carried out under nitrogen atmosphere (Air Liquid) by bubbling 1 mL/min into the cell and all experiments were duplicated.

By comparing the CVs obtained in the absence and presence of hydrogen peroxide, the onset potential (E_{onset}) for first reduction and oxidation was obtained. Also, the *Tafel* slope for both processes, called as b, and the current exchange (i_o) were calculated from the overpotential ($E - E_{ocp}$) *vs.* log (I) plots for each test using the following equation:

$$(E - E_{ocp}) = m + 2.30 \times b \times \log(I) \quad (1)$$

2.4. Hydrogen peroxide decomposition with carbon catalysts

The reactions were carried out batch-wise in a magnetically stirred three-necked glass reactor equipped with a reflux condenser. The operating conditions were selected according to a previous work [19]. In a typical experiment, 45 mL of distilled water at pH = 3.5 (HCl, Sigma–Aldrich) was placed in the flask together with 0.125 g powdered catalyst. The content was heated to 80 °C (IKA RCT basic). Once this temperature had been reached, 5 mL of 250 g/L hydrogen peroxide (Sigma–Aldrich) was injected and the content stirred at 1200 rpm. After a reaction time of 2 h the heating was switched-off and the flask cooled to room temperature in cold water. Finally, the catalyst was separated by filtration (0.45 μm Nylon filter) and oven-dried at 60 °C.

3. Results and discussion

3.1. Characterization study

Table 1 summarizes the structural characteristics of the carbons obtained from XRD, the BET and external surface area, ash and Fe content, and the amount of CO_2 and CO evolved upon TPD analysis.

The values of the structural parameters in Table 1, such as the interlayer spacing (d_{002}), average crystalline height (L_c), and average crystalline diameter (L_a), were calculated from the XRD patterns (shown in Fig. S1 of the Supplementary Material). The calculated d_{002} values confirm the amorphous character of activated carbons, AC-M and AC-P. Conversely, the G-S and G-F samples, present a highly ordered structure as indicated by the d_{002} close to the value of graphite (3.354 Å). While the carbon blacks, CB-C and CB-V, exhibit intermediate values in the XRD parameters. The lower d_{002} and higher L_c and L_a values of CB-C indicate a more ordered structure compared with CB-V.

The S_{BET} values calculated from the N_2 adsorption/desorption isotherms at 77 K (Fig. S2 of the Supplementary Material) demonstrate that activated carbons, AC-M and AC-P, present a highly developed porosity whereas the carbon blacks, CB-C and CB-V, and even more so, the graphites, G-S and G-F, show substantially lower values of surface area without microporosity contribution, except in the case of the CB-V carbon black. Differences in the distribution of porosity can be observed between the activated carbons, showing AC-P a substantially higher contribution of mesoporosity.

The ash content of the carbon materials tested is, in general, quite low, except in the case of the as-received activated carbon AC-M (4%). It is important to know the content of iron of the ashes because of its catalytic activity for hydrogen peroxide decomposition enhancing the ability of activated carbon in this reaction [3,10–13,20]. For this reason, the iron content was quantified (Table 1). Unexpectedly, G-S had the highest amount of Fe (0.44%) whereas the presence of this metal in the other materials was negligible. Regarding the surface composition, the amount of CO_2 and CO evolved, as obtained from the integration of the TPD curves, (Fig. S3 of the Supplementary Material) are shown in Table 1. As expected, the two activated carbons show the highest content of surface oxygen groups (SOG) as a result of the activation process.

Summarizing, three different types of carbons have been studied. Activated carbons, which are amorphous materials with a developed porous structure and significant amounts of surface oxygen groups; graphites, which have the opposite characteristics because they are almost crystalline materials, with a very low specific surface area and scarce surface oxygen groups; carbon blacks, with structural, textural and chemical features in between the two.

The effect of those characteristics on the catalytic behavior of activated carbons for hydrogen peroxide decomposition has been widely studied in the literature [1,4–6,8,10–14]. Some of these studies conclude that disordered structures with less

developed graphitic layers have a higher concentration of electron-rich centers promoting hydrogen peroxide decomposition [3,7]. However, the more disordered the structure, the more surface oxygen groups. In general, acid SOG reduce the reactivity of the activated carbons due to their electron withdrawal capacity [1,5–7,12,14] whereas basic SOG are always beneficial [4,8]. On the one hand, the diffusion of the reagents toward the active sites is favored by the hydrophilic character of the carbon material, a feature controlled by the acid SOG [21], in the presence of a sufficiently developed mesoporosity [22]. By contrast, carbon materials with a highly ordered structure such as graphites have electronic and conductive properties which can favor the electron transfer between these materials and hydrogen peroxide [12].

In general, carbon materials have a wide diversity of characteristics which would hinder a predictive approach of their activity for hydrogen peroxide decomposition as coupled effects frequently exist. In this context our proposal is that voltammetry measurements are a useful tool for the assessment of the activity of carbon materials in the aforementioned reaction. In that respect, the starting and modified carbon materials collected in Table 1 provide a series of widely different samples for testing.

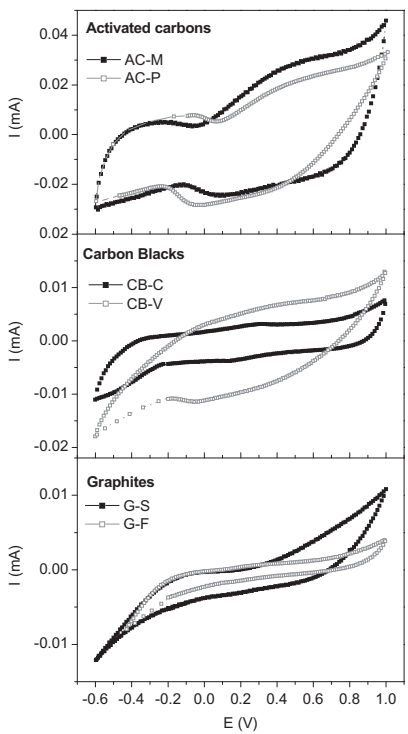

Fig. 2 – Cyclic voltammograms of carbon materials in the absence of hydrogen peroxide (background). Operating conditions: v = 10 mV/s, T = 25 °C, pH = 3.5 (HCl).

3.2. *Carbon voltammetry experiments*

Fig. 2 depicts the unchanging cyclic voltammograms in the background solution (pH = 3.5, HCl) for each type of carbon. When the applied potential changes to a negative direction (reduction scan), a gradually increasing negative current was measured; in the same way, if the potential went in a positive direction, the positive current increases and the oxidation process takes place. None of the cyclic voltammograms recorded were totally symmetrical. This fact led us to believe that the carbon materials include not only purely capacitive, but also electro-active species (viz. surface oxygen groups, heteroatoms or ashes) with redox properties.

The coulombic charge (CC), calculated from the background voltammograms, varied according to the specific surface area of the materials: AC > CB > G and a linear relationship between this parameter (CC) and S_{BET} has been found as can be seen in Fig. 3. The higher the surface area, the more active sites (electron-rich locations on the carbon surface), and so, an increased coulombic charge can be expected. Eventually, cyclic voltammetry could be used for specific surface determination of carbon materials.

Additional cyclic voltammetry experiments were carried out in presence of hydrogen peroxide with the purpose of analyzing the electrochemical behavior of carbons when in contact with that electroactive reactant. The E_{ocp} values recorded before the potential application are given in Table 2 and the voltammograms are shown in Fig. 4. The E_{ocp} values, ranged from 0.413 to 0.499 V, being within the thermodynamic reduction/oxidation potentials of hydrogen peroxide (−0.905 and 1.566 V, respectively, Ag/AgCl) and correspond with a mixed potential. The oxidation and reduction current intensities measured in the presence of hydrogen peroxide (Fig. 4) are clearly higher than those in the absence of it (Fig. 2). The carbon that exhibits the maximum ability for the reduction step also shows the maximum for the oxidation step. It is noteworthy the crossover loops observed in the former. These hysteresis loops observed in both oxidation and reduction directions, indicate that the carbon surface is irreversibly modified upon cyclic voltammetry when hydrogen

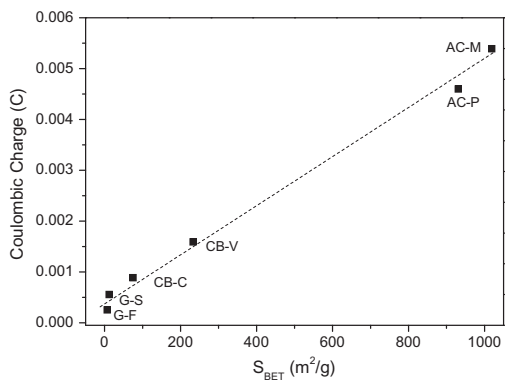

Fig. 3 – Relationship between S_{BET} and coulombic charge. Operating conditions: v = 10 mV/s, T = 25 °C, pH = 3.5 (HCl).

Table 2 – Electrochemical properties of the carbon materials tested.

Sample	E_{ocp}	Reduction process		Oxidation process		i_o
		E_{onset}	b	E_{onset}	b	
	(V)	(V)	(V/decade)	(V)	(V/decade)	(A/g)
AC-M	0.460	0.094	−0.437	0.513	0.276	0.232
AC-M-HCl	0.489	0.022	−0.393	0.575	0.227	0.125
AC-P	0.413	0.057	−0.434	0.690	0.307	0.147
AC-P-HNO_3	0.461	0.050	−0.443	0.686	0.294	0.121
CB-C	0.493	0.050	−0.398	0.559	0.219	0.060
CB-V	0.430	0.024	−0.426	0.679	0.344	0.137
G-S	0.492	0.086	−0.454	0.520	0.264	0.172
G-S-HCl	0.499	0.045	−0.342	0.629	0.261	0.099
G-F	0.420	0.009	−0.375	0.587	0.211	0.052

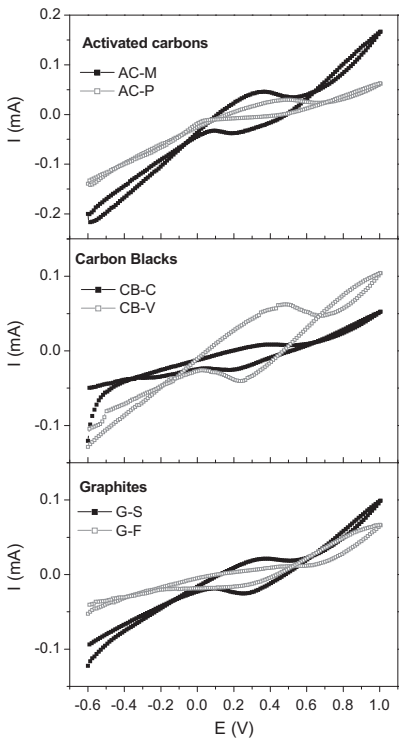

Fig. 4 – Cyclic voltammograms of carbon materials in presence of hydrogen peroxide. Operating conditions: v = 10 mV/s, T = 25 °C, pH = 3.5 (HCl), $C_{H_2O_2}$ = 25 g/L.

peroxide is in the media. At 1 V potential value, the carbon surface has been deeply oxidized by the effect of the going sweep and the created SOGs contribute to a more effective hydrogen peroxide oxidation upon the reverse scan. Then, currents registered are higher than those values measured in the going sweep, resulting in the first hysteresis loop. The irreversible oxidation of the carbon surface upon cyclic voltammetry also disfavors the reduction of hydrogen peroxide. As a consequence, a lower reduction current is obtained in the reverse scan, from −0.1 to −0.6 V, and the second hysteresis loop observed. Therefore, these findings suggest that the regeneration of the carbon active sites (step 2 in Fig. 1) is expected to be the limiting reaction.

Several electrochemical parameters viz. E_{onset}, *Tafel* slopes and i_o were calculated from the voltammograms (see Section 2). The values are summarized in Table 2.

The E_{onset} values for hydrogen peroxide reduction were close to 0 mV for all the carbons tested, while for oxidation more variable values were obtained, ranging from 0.513 to 0.690 V. The *Tafel* slope values corresponding to hydrogen peroxide reduction were between −0.375 and −0.454 V/decade, while for oxidation, the range covered from 0.211 to 0.344 V/decade (Table 2). These relatively high values indicate that hydrogen peroxide decomposition over carbon materials is a complex process, which in addition to the charge transfer, other phenomena, like adsorption/desorption, must be involved. Furthermore, the fact that the *Tafel* slopes were quite similar for all the carbon materials tested, suggests that the reaction mechanism does not vary from one material to another.

According to the current exchange values, i_o (the most representative parameter in electrochemical reactions, Table 2), the activity of carbon materials in the cyclic voltammetry experiments follows the order: AC-M > G-S > AC-P > CB-V > CB-C > G-F. The lowest activity of G-F is consistent with the characterization results in Table 1 which show that this carbon material has the lowest surface area and no iron content. Nevertheless, the voltammetry results indicate that AC-M, and unexpectedly, G-S, are electrochemically more active than AC-P. In the case of G-S, the explanation could be that the effect of the iron content prevails over that of surface area (or its equivalent electrochemical parameter, the coulombic charge, according to Fig. 3). To confirm the important effect of iron on the electrochemical carbon capacity, the cyclic voltammetry response of G-S-HCl sample was compared to that of G-S in Fig. 5 (Fe content equal to 0.02 and 0.44 wt%, respectively, see Table 1). The decrease in the reduction E_{onset} and the increase in the oxidation one of G-S-HCl with respect to the starting G-S (see values in Table 2) indicate a diminished

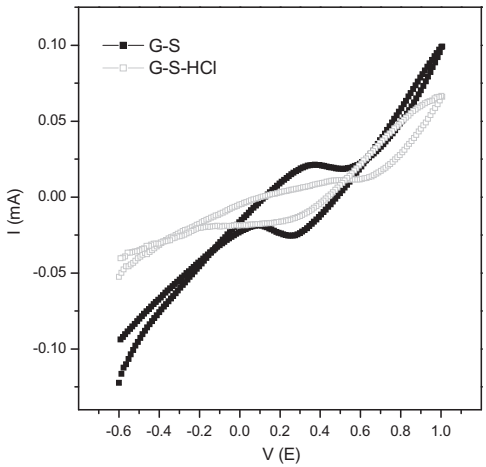

Fig. 5 – Effect of Fe content on the cyclic voltammetry response of G–S carbon. Operating conditions: v = 10 mV/s, T = 25 °C, pH = 3.5 (HCl), $C_{H_2O_2}$ = 25 g/L.

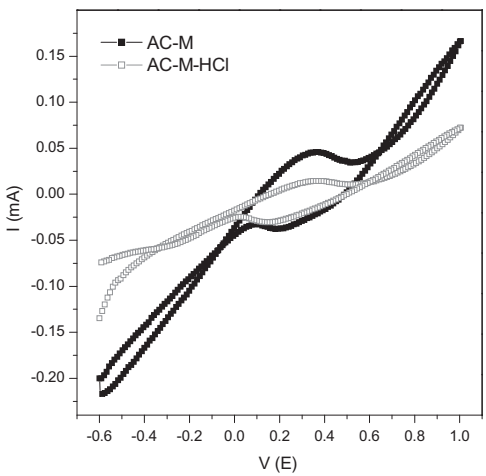

Fig. 6 – Effect of ash-content reduction on the cyclic voltammetry response of AC-M carbon. Operating conditions: v = 10 mV/s, T = 25 °C, pH = 3.5 (HCl), $C_{H_2O_2}$ = 25 g/L.

electrochemical capacity of the former, supporting the initial hypothesis.

In the case of AC-M and AC-P, the iron content must have only a negligible effect because it is very low in both cases. However, other features such as the ash content and the amount of surface oxygen groups could explain their different electrochemical behavior. AC-M is the carbon tested with highest ash content by far (see Table 1). Among the elements identified by TXRF were Fe, Ti, Ca and Cu. The ash

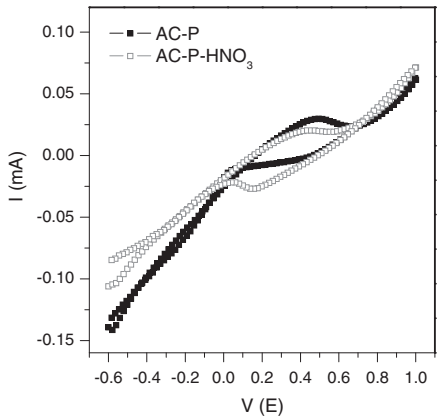

Fig. 7 – Effect of surface oxygen groups content on the cyclic voltammetry response of AC-P carbon. Operating conditions: v = 10 mV/s, T = 25 °C, pH = 3.5 (HCl), $C_{H_2O_2}$ = 25 g/L.

content was reduced by more than half after HCl treatment (see AC-M and AC-M-HCl in Table 1). The corresponding voltammogram obtained in presence of hydrogen peroxide is given in Fig. 6 and the results (see i_o values in Table 2) show a decrease in the electrochemical capacity of AC-M after reduction of the ash content.

To investigate the influence of surface oxygen groups, the AC-P carbon was oxidized with HNO_3 and a voltammogram of the resulting modified carbon (AC-P-HNO_3) obtained (Fig. 7). HNO_3 oxidation substantially increased the amount of SOG (see Table 1) and the voltammetry results (Fig. 7 and Table 2) indicate a decrease in the electrochemical capacity of the carbon. According to the shape of the voltammograms (Fig. 7), the decline is more pronounced in the reduction reaction than in the oxidation reaction, because the former is more affected by the decrease of the electronic density of the basal planes, caused by the presence of the acid oxygen groups.

In conclusion, AC-M showed a higher electrochemical activity than AC-P because of its higher ash content and lower amount of acid SOG.

3.3. *Catalyst screening*

The decomposition of hydrogen peroxide is assumed to follow pseudo-first-order kinetics [5,7,8,14]:

$$-\frac{dC_{H_2O_2}}{dt} = k_d \times C_{H_2O_2} \quad (2)$$

where k_d represents an apparent kinetic constant which includes several parameters such as temperature, catalyst concentration, and pH. Fig. 8 shows the plot of ($\ln C_{H_2O_2}$) vs. reaction time for the carbon materials tested. The values of the apparent kinetic constant are given in Table 3 together with the corresponding correlation coefficients which confirm the validity of the simple rate equation used. According to these results, the activity of the carbons tested follows the same order as that previously found using voltammetry

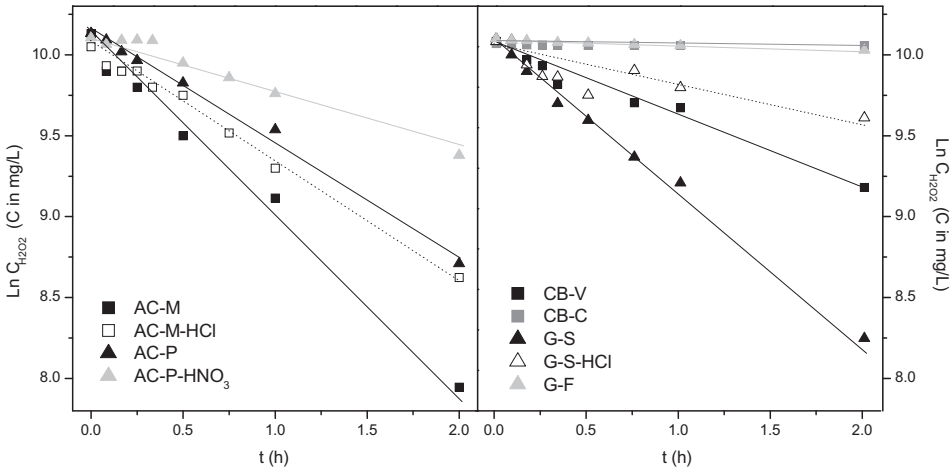

Fig. 8 – First-order plots of hydrogen peroxide decomposition with the carbon materials. Operating conditions: T = 80 °C, pH = 3.5 (HCl), C_{carbon} = 5 g/L $C_{H_2O_2}$ = 25 g/L.

Table 3 – Values of the apparent first-order rate constant for hydrogen peroxide decomposition with the carbons tested.

Sample	k_d (h^{-1})	r^2
AC-M	1.005	0.993
AC-M-HCl	0.637	0.986
AC-P	0.571	0.983
AC-P-HNO_3	0.370	0.995
CB-C	0.032	0.999
CB-V	0.424	0.978
G-S	0.869	0.997
G-S-HCl	0.203	0.995
G-F	0.049	0.966

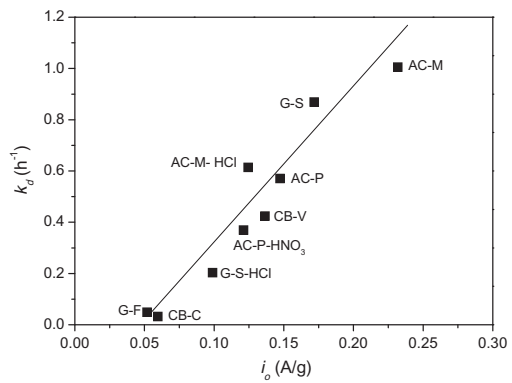

Fig. 9 – Relationship between the exchange current (i_o) and apparent first-order rate constant (k_d) for hydrogen peroxide decomposition with the carbons tested.

measurements. Also, the activity of the modified carbons is lower than those of their corresponding starting ones (Table 3).

A linear relationship has been found between the exchange current (i_o) (Table 2) and the decomposition rate constants (k_d) (Table 3) as shown in Fig. 9. As can be seen, this relationship also applies to the modified carbons. Therefore, the electrochemical capacity of carbons, which is a measurable property in cyclic voltammetry, can be used to predict the activity of the carbon materials in hydrogen peroxide decomposition. According to these results, and further investigations being carried out in this laboratory, the outlook for the potential application of this technique to evaluate the activity of carbon materials in redox reactions in general is quite promising.

4. Conclusions

It has been proved that cyclic voltammetry provides a rapid, direct, and useful technique for predicting the catalytic activity of carbon materials for hydrogen peroxide decomposition. The exchange current, determined by the voltammograms, is an overall variable governing carbon activity. A linear dependence has been obtained between both.

Cyclic voltammetry also enables a greater insight into the catalytic behaviour because it becomes clear that the limiting step in hydrogen peroxide decomposition with carbon materials, is the regeneration of the active sites upon carbon reduction.

Applying the electrochemical characterization to a number of carbon materials of widely different physico-chemical characteristics provided an understanding of the effects of those features on the catalytic activity for hydrogen peroxide decomposition. The results indicate that the most important factor in the catalytic activity is the content of metals, in particular iron, this is followed by the specific surface area and finally the content of surface oxygen groups.

Acknowledgments

The authors wish to thank the Spanish MICINN for the financial support for the projects CTQ2008-03988/PPQ, CTQ2010-14807 and S2009/AMB-1588. Our gratitude to the anonymous reviewer for his/her helpful comments and recommendations which have significantly contributed to improve the quality of the paper.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.03.058.

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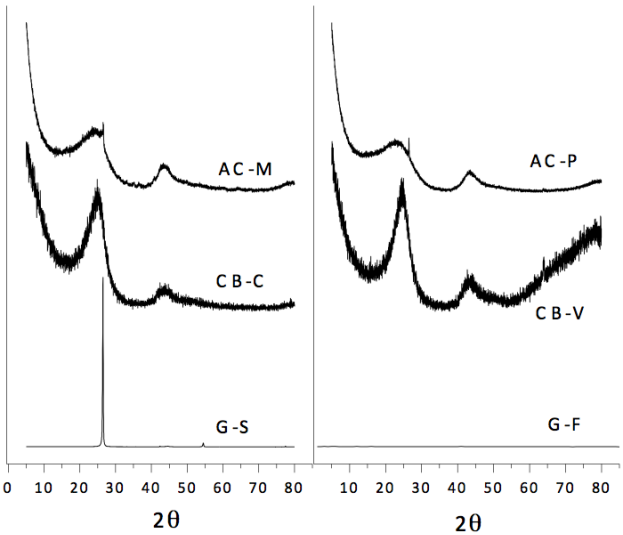


Figure S1. X-ray diffraction profiles of the carbon materials.

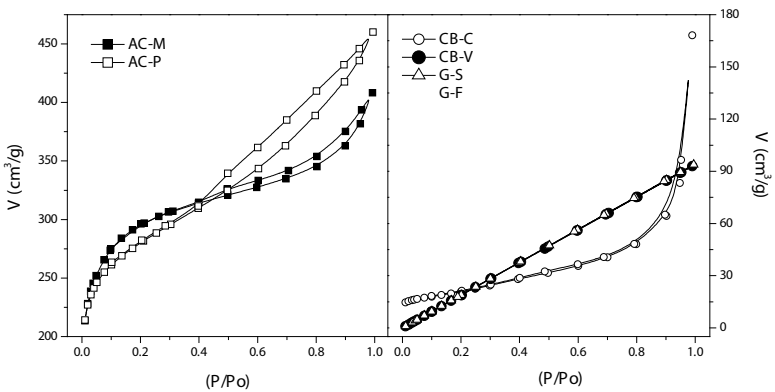


Figure S2. 77 K N2 adsorption/desorption isotherms of the carbon materials.

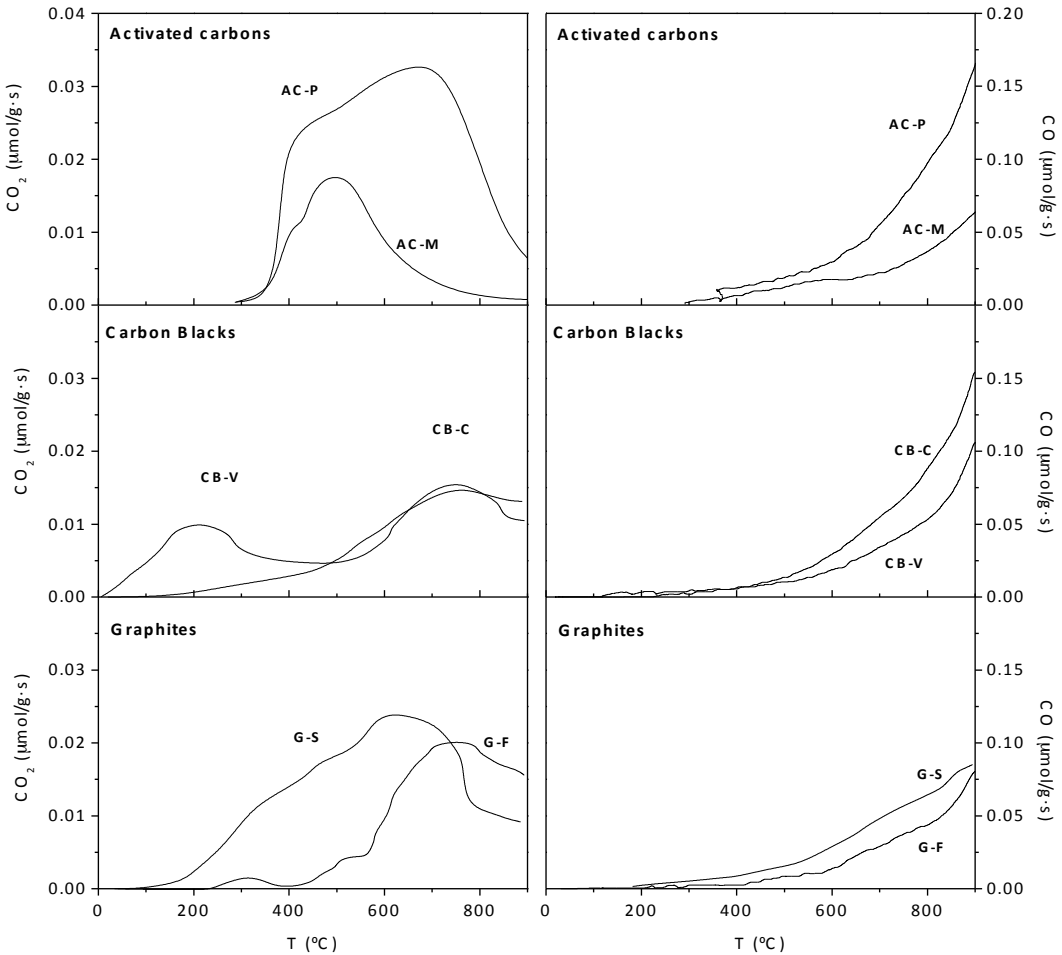
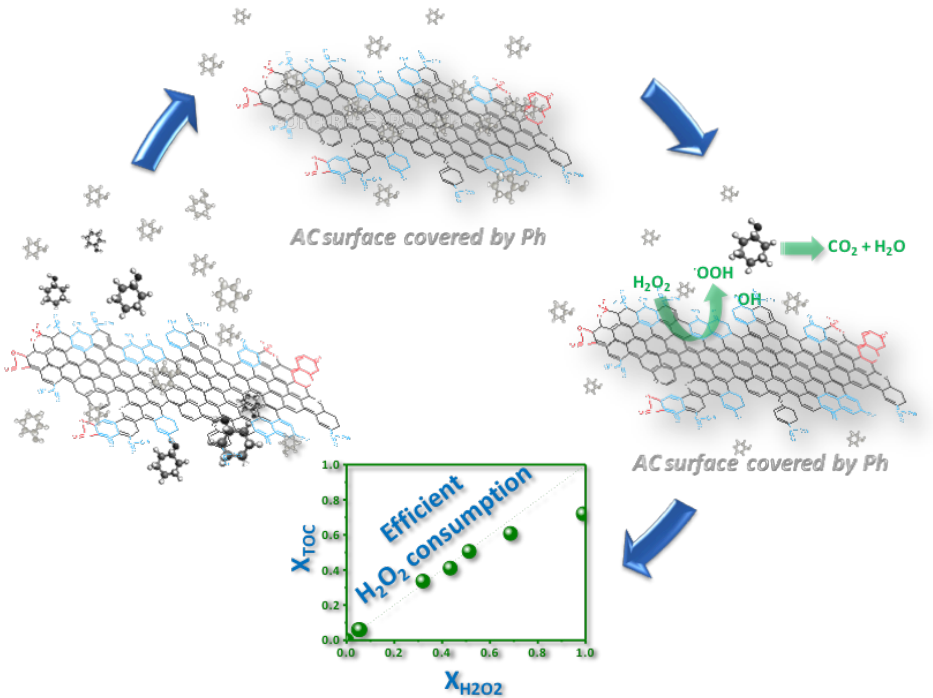


Figure S3. TPD profiles of the carbon materials.

Capítulo IV. Highly efficient application of activated carbon as catalyst for wet peroxide oxidation



Applied Catalysis B: Environmental 140–141 (2013) 663–670

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Highly efficient application of activated carbon as catalyst for wet peroxide oxidation

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ARTICLE INFO

Article history:
Received 20 February 2013
Received in revised form 27 April 2013
Accepted 30 April 2013
Available online 8 May 2013

Keywords:
Activated carbon
Hydrogen peroxide
Cyclic voltammetry
Catalytic wet peroxide oxidation
Regeneration

ABSTRACT

This paper addresses the improved performance of activated carbons in catalytic wet peroxide oxidation (CWPO) of phenol as target compound. Initial cyclic voltammetry experiments show that hydrogen peroxide and phenol compete for the same active sites on the carbon surface. Then, a significant coverage of the carbon surface by phenol molecules is the approach attempted to increase the efficiency of hydrogen peroxide and the performance of the oxidation process.

In this work, two commercial activated carbons, with different physical and electrochemical properties have been tested. The results demonstrate that working at high phenol concentration (5 g/L) and phenol/carbon mass ratio (2), unprecedented hydrogen peroxide efficiencies of around 100% are achieved, allowing high oxidation and mineralization degrees, *i.e.* 97% phenol and 70% TOC conversions at 80 °C with the stoichiometric dose of hydrogen peroxide required for complete mineralization of phenol. The oxidation route of phenol in the presence of activated carbon is also studied and a reaction pathway proposed. Resorcinol was a new by-product detected whose formation occurs upon reaction on the carbon surface. Condensation by-products, typically formed in Fenton oxidation of phenol, were not found in the effluents but adsorbed on the carbon surface causing a progressive deactivation upon use. The activity can be easily recovered by oxidative thermal regeneration (350 °C, 24 h).

1. Introduction

Catalytic wet peroxide oxidation (CWPO) relies on the oxidation of organic pollutant in water under relatively mild operating conditions (T = 25–100 °C, P = 0.1–0.5 MPa) using hydrogen peroxide as oxidant.

Activated carbons (ACs) have been used as catalysts in CWPO [1–11] since they exhibit donor–acceptor surface properties allowing hydrogen peroxide decomposition into radical species through an electron transfer reaction similar to the Fenton mechanism [12,13]. In this way, AC and AC^+ act as reduced and oxidized catalyst states leading to the formation of •OH and •OOH, respectively [4,5,8,10,14,15]. As studied in a previous work [16], the electrochemical capacity of a carbon material dictates the carbon activity in this reaction. Cyclic voltammetry analysis combined with kinetic studies have shown that the apparent first-order rate constant for hydrogen peroxide decomposition is linearly dependent on the exchange current, and that the limiting step in this reaction is the regeneration of the active sites by the reduction of the carbon surface.

In spite of the widely demonstrated ability of activated carbons for hydrogen peroxide decomposition, the removal of organic pollutants in CWPO with bare ACs proceeds mostly through adsorption [1,2,11,13]. Low activities for removal of phenolic compounds [2,8,9,11] and moderate for dyes [3–5,7] have been usually observed even at hydrogen peroxide doses significantly higher than the stoichiometric ones for the complete mineralization of phenol. The efficient consumption of hydrogen peroxide is of main concern in CWPO with activated carbons. AC promotes parasitic reactions consuming •OH and •OOH radicals to produce oxygen, a non-effective specie under the temperature range commonly used in wet peroxide oxidation. That represents a serious drawback for the potential application of AC in CWPO. For this reason, transition metals, in particular Fe, and metal oxides have been incorporated onto the carbon surface. The high surface area of activated carbons provides multiple anchoring sites for the metal and a high capacity for the adsorption of organic molecules. However, metal leaching has been commonly observed.

A different approach to improve the performance of ACs has been attempted through chemical modification of the carbon surface addressed to introduce acid or basic oxygen groups

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http://dx.doi.org/10.1016/j.apcatb.2013.04.068

[3–5,7,9]. According to some results, acid groups decrease the activity of the virgin AC for hydrogen peroxide decomposition [5–7,9,15,17], while the incorporation of basic groups does the opposite [4,11,15,17]. In both cases, oxidation is enhanced but obviously due to different effects. The acid groups with electron withdrawal capacity substrate electrons from the basal planes of the carbon surface thus restricting their availability to hydrogen peroxide molecules. Therefore, radical species from hydrogen peroxide are formed more gradually and the extension of the parasitic reactions decreases while increasing the breakdown of organic species [9]. On the other hand, basic groups (pyrones, chromenes, ethers and carbonyls) enhance the decomposition of hydrogen peroxide into radicals species.

Herein, we offer a novel approach to enhance the selectivity of AC toward phenol oxidation and mineralization in detriment of the scavenging reactions, with the aim of maximizing the efficiency of hydrogen peroxide consumption. This approach consists of carrying out the CWPO at relatively high phenol concentration (5 g/L), substantially above the most commonly used and also, high phenol/carbon mass ratio. Then, a significant coverage of the carbon surface by the organic molecules should decrease the rate of radical formation from hydrogen peroxide decomposition and makes phenol more easily available to the oxidizing radicals. Both aspects reduce the occurrence of parasitic scavenging reactions on the carbon surface.

Two commercial activated carbons with different physical and electrochemical properties have been tested in CWPO using phenol as target compound. Their activity has been evaluated in relation with hydrogen peroxide decomposition and phenol oxidation and mineralization. Also, the phenol oxidation pathway in the presence of activated carbon has been investigated. Regeneration of the activated carbon after its use has been studied as well.

2. Experimental

2.1. Reagents

Aqueous phenol solutions were prepared with phenol (5 g/L) (Sigma–Aldrich) at pH 3.5 using HCl 1 M (Panreac). Hydrogen peroxide solution (30% w/w) was purchased from Sigma–Aldrich. Working standard solutions of phenol (Sigma–Aldrich), hydroquinone (Sigma–Aldrich), resorcinol (Sigma–Aldrich), catechol (Sigma–Aldrich), *p*-benzoquinone (Sigma–Aldrich), acetic acid (Sigma–Aldrich), formic acid (Sigma–Aldrich), malonic acid (Sigma–Aldrich), maleic acid (Sigma–Aldrich) and oxalic acid (Panreac) were prepared for equipment calibration. Other reagents used in the analysis were H_2SO_4 (Panreac), C_2H_3N (Riedel-deHaën), Na_2CO_3 (Panreac), $NaHCO_3$ (Merck), $Na_2S_2O_8$ (Panreac), HPO_4 (Fisher), $C_6H_4COOHCOOK$ (Aldrich), $TiOSO_4$ (Riedel-deHaën), $C_{16}H_{18}N_3ClN_3S$ (Panreac) and CH_3OH (Sigma–Aldrich). These reagents are of analytical grade and were used without further purification. All the solutions were prepared with milli-Q water.

2.2. Activated carbons

Commercial activated carbons were supplied by Merck (AC-M, ref.: 102514, granular) and Panreac (AC-P, ref.: 121237, $d_p < 100\ \mu m$). Before use they were sieved to yield a particle size ranged from 80 to 100 μm. Also, the samples of activated carbons were pre-washed with a phenol solution by contacting 0.125 g of AC with 50 mL of the 5 g/L phenol solution at 80 °C during 24 h under vigorous stirring. The resulting samples were identified as w-AC-P and w-AC-M.

2.3. Characterization of the activated carbons

Different techniques were used for the characterization of the ACs used as catalysts. X-ray diffraction (XRD) was performed in a Siemens Model D5000 X-ray diffractometer, using Cu Kα (8.04 keV) radiation, and a step of 0.02°/s for $2\theta = 5°–100°$. XRD data were analyzed with PDF 2000 (JCPDS-ICDD) software.

Thermogravimetric analysis (TGA) was carried out in a Mettler-Toledo TGA/SDTA851^e thermobalance. The sample powders were heated in air from 50–900 °C at heating rate of 10 °C/min. The textural properties of fresh and pre-washed carbons were characterized from the 77 K N_2 adsorption/desorption isotherms using a Micromeritics Tristar apparatus, outgassing the samples overnight at 150 °C to a residual pressure of $<10^{-3}$ Torr. The external or non-microporous surface area (A_{ext}) and the micropore volumes (V_m) were calculated by the *t*-method. Elemental analysis was performed in a LECO Model CHNS-932 apparatus. Total reflection X-ray fluorescence (TXRF) (Extra-II Rich & Seifert spectrometer) was used for elements identification and iron content in the carbon ashes. The surface oxygen groups (SOGs) were quantified by temperature-programmed desorption (TPD). The analysis was carried out as follows: a sample of 100 mg of carbon was placed in a quartz tube and heated at 10 °C/min from room temperature up to 900 °C. N_2 was used as carrier gas at 1000 N mL/min. The evolving CO_2 and CO were analyzed in a SIEMENS (mod. Utramat 22) gas analyzer. Deconvolutions of the TPD spectra were adjusted to multiple Gaussian function by Peakfit 4.12 software.

Cyclic voltammetry measurements were carried out at room temperature and ambient pressure in a conventional three-electrode electrochemical cell, using a computerized potentiostat (Autolab PGSTAT 302, Eco Chemie) controlled by GPES software. A glassy carbon rotating disk electrode was used as substrate for the carbon samples, a gold electrode as the counter electrode, a saturated Ag/AgCl, KCl electrode as the reference and HCl solution (pH 3.5) as electrolyte. The carbon electrode was prepared by dispersing 6 mg of the activated carbon (as-received or pre-washed with a phenol solution) in Milli-Q water (730 μL) with ultrasonic agitation (Hyelscher, UP50H) and dropped on the glassy carbon electrode (20 μL) to obtain a uniform catalyst film. The prepared electrodes were subjected to cyclic voltammetry measurements (10 mV/s) under nitrogen atmosphere in the absence (background) and the presence of hydrogen peroxide (25 g/L) within the potential range from −0.6 to 1 V. From these experiments, the coulombic charge (*CC*) and the exchange current (i_o) were calculated. More detailed description of this analysis has been reported elsewhere [16].

2.4. Wet peroxide oxidation experiments

The oxidation tests were carried out batch-wise in a magnetically stirred three-necked glass reactor equipped with a reflux condenser. In a typical experiment, 45 mL of aqueous phenol solution (5 g/L) at pH 3.5 (HCl) were placed in the reactor, along with 0.125 g of activated carbon and the content was heated to 80 °C. Once this temperature was reached, 5 mL of an adjusted concentration of hydrogen peroxide solution were injected and the stirring at 1200 rpm started. Effluents at different reaction times were taken from the reactor and immediately analyzed. After 24 h of reaction, the heating was switched-off and the flask cooled to room temperature in cold water. Then, the catalyst was separated by filtration (0.45 μm Nylon filter) and oven-dried at 60 °C. Additionally, homogenous contribution was assessed by working in the absence of catalyst (blank experiment). Hydrogen peroxide decomposition experiments with activated carbons in the absence of phenol were also carried out. Adsorption runs were performed under the same operating conditions and procedure as the oxidation tests but in the

Table 1
Characterization of the activated carbons.

Sample	d_{002} (Å)	L_c (Å)	L_a (Å)	S_{BET} (m^2/g)	A_{ext} (m^2/g)	V_m (m^3/g)	CO_2 (μmol/g)	CO (μmol/g)
AC-M	3.61	37.99	17.67	1019	175	0.38	30	320
w-AC-M	–	–	–	416	147	0.11	255	483
AC-P	3.79	35.99	16.22	931	472	0.19	131	730
w-AC-P	–	–	–	489	252	0.11	219	674
4th use AC-P	–	–	–	302	264	0.04	1358	2565
Reg. AC-P	–	–	–	920	443	0.22	535	4741

absence of hydrogen peroxide. All the experiments were performed by triplicate being the standard deviation always less than 5%.

2.5. Analytical methods

The organic compounds in the effluent were identified and quantified by high performance liquid chromatography (HPLC, Varian, Mod. ProStar) and ionic chromatography (IC, Metrohm, mod. 883 BASIC IC Plus). Phenol and the aromatic intermediates resulting from oxidation were separated by a Nucleosil C18 5 mm column (Microsob-MV, 15 cm long, 4.6 mm diameter) using a mixture of 4 mM H_2SO_4 aqueous solution at 1 mL/min as mobile phase. A diode array detector at wavelengths of 210 and 246 nm was used. Short-chain organic acids were determined by IC with anionic chemical suppression using a conductivity detector. A Metrosep A supp 5–250 column (25 cm long, 4 mm diameter) was used as stationary phase and 0.7 mL/min of an aqueous solution 3.2 mM of Na_2CO_3 and 1 mM of $NaHCO_3$ as mobile phase. Total organic carbon (TOC) was measured in a Shimadzu TOC V_{SCH} analyzer. Metal content in the liquid effluent was analyzed by TXRF. Hydrogen peroxide concentration was quantified by colorimetric titration using the titanium sulfate method [18]. The presence of hydroxyl radicals was visualized by the methylene blue dye test. Effluents at different reaction times were drop-sampled on a blue methyl tip prepared according to Satoh et al. protocol [19]. The bleaching of the tip corresponds to the oxidation of methylene blue dye (dark blue color) to methyl blue radical cation (colorless) by the hydroxyl radicals.

3. Results and discussion

3.1. Activated carbon characterization

Table 1 collects some structural and textural characteristics of the activated carbons, along with the amounts of CO and CO_2 evolved upon TPD. The elemental analysis results are summarized in Table 2. The corresponding XRD, BET isotherms and TPD profiles are supplied in Figs. S1–S3 of Supporting Information.

Looking at the values of the parameters calculated from the XRD profiles (see Supporting Information, Fig. S1), namely the interlayer spacing value (d_{002}) and the height (L_c) and width (L_a) of the crystalline domains, given in Table 1, both activated carbons are amorphous materials but with different level of disorder. The lower d_{002} and higher L_a and L_c values of AC-M indicate a less-disordered carbon structure than that of AC-P.

Table 2
Elemental analysis of the activated carbons (%, dry bases).

Sample	C	H	N	S	Ashes[a]	O[b]
AC-M	89.3	0.9	0.5	0.6	4	4.7
AC-P	93.7	0.8	0.3	0.1	1	4.1
4th use AC-P	81.0	1.8	0.2	0.06	1	15.9
Reg. AC-P	74.5	2.1	0.2	0.05	1	22.2

[a] Data provided by the supplier.
[b] Calculated by difference.

The textural analyses from N_2 adsorption–desorption isotherms (provided in Supporting Information, Fig. S2) indicates that both carbons have close values of BET surface area but AC-P shows significantly higher contribution of mesoporosity according to the values of the external or non-microporous area (A_{ext}) and the micropore volume (V_m). With regard to chemical composition, the main differences arise from the amount of surface oxygen groups (Table 1) and the ash-content (Table 2), higher in the case of AC-P and AC-M, respectively. Several metallic elements (Ca, Ti, V, Cr, Fe) were identified in the ashes by TXRF, being the content of Fe quite low, 0.04 wt% for AC-M and 0.01 wt% for AC-P. These metallic elements, in particular Fe, must be taken into consideration due to their catalytic effect on hydrogen peroxide decomposition [16]. After phenol prewashing both carbons showed significantly lower BET surface area as a consequence of phenol adsorption, which reduces the available surface for N_2. The micropore volume was significantly reduced after this treatment in the case of w-AC-M but in a much less extent in the case of w-AC-P indicating that the latter maintains the micropores accessible, likely thanks to the most developed external area.

3.2. Hydrogen peroxide decomposition

In a previous work [16], the activity of carbon materials, *viz.* activated carbons (*i.e.* AC-M and AC-P), carbon blacks and graphites for hydrogen peroxide decomposition was evaluated through the values of the apparent first-order rate constant (k_d) and a linear dependence was found between those values and the exchange current (i_o) measured by cyclic voltammetry (see Fig. S4 of Supporting Information). The results demonstrated the supremacy of AC-M over AC-P, exhibiting the former twice the activity of the second because the effect of metallic species (most in particular Fe) prevails over the other physico-chemical features.

Herein, to learn more on the catalytic activity of the activated carbons for hydrogen peroxide decomposition in CWPO, cyclic voltammetry measurements of ACs with phenol adsorbed (w-AC-M and w-AC-P) were now programmed, with the purpose of reproducing the surface conditions in CWPO. The voltammograms are given in Figs. 1 and 2, along with those previously reported for fresh AC-M and AC-P [16] for the sake of comparison. The values of coulombic charge (*CC*), calculated from the background area of the voltammograms displayed in Fig. 1, and those of the exchange current (i_o), calculated from Fig. 2, are collected in Table 3. Interestingly, the coulombic charge of w-AC-M and w-AC-P decreased

Table 3
Electrochemical properties of the activated carbons and values of the first-order rate constant for hydrogen peroxide decomposition.

Sample	Coulombic charge (mC)	i_o (A/g)	k_d (L/h g)	r^2
AC-M	5.93	0.232	0.420	0.993
w-AC-M	1.42	0.073	0.067	0.992
AC-P	4.60	0.147	0.228	0.983
w-AC-P	1.37	0.045	0.034	0.979
4th use AC-P	1.08	0.017	0.007	0.981
Reg. AC-P	3.37	0.157	0.281	0.991

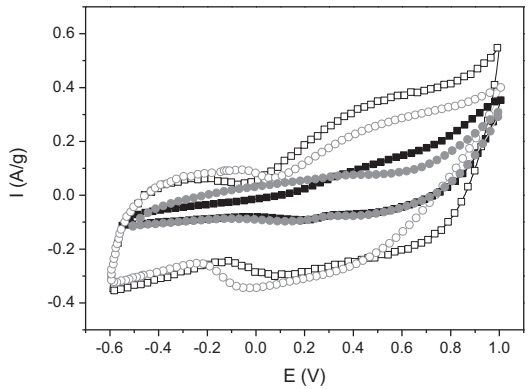

Fig. 1. Cyclic voltammograms of the fresh and pre-washed activated carbons. Operating conditions: $v = 10$ mV/s, $T = 25$ °C, pH 3.5 (HCl); (□) AC-M, (■) w-AC-M, (○) AC-P, (●) w-AC-P.

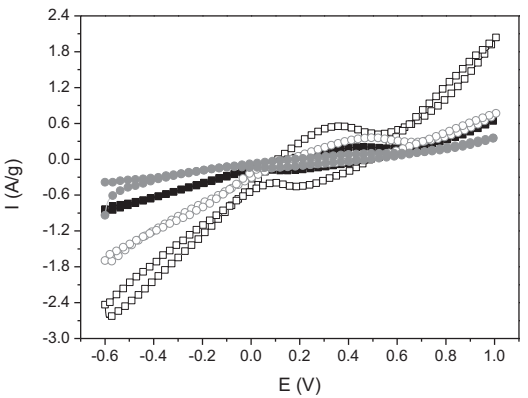

Fig. 2. Cyclic voltammograms of activated carbons in the presence of hydrogen peroxide. Operating conditions: $C_{H_2O_2} = 25$ g/L, $v = 10$ mV/s, $T = 25$ °C, $pH = 3.5$ (HCl); (□) AC-M, (■) w-AC-M, (○) AC-P, (●) w-AC-P.

around 70% with respect to the fresh carbons (Table 3). This reduction must be associated with the adsorbed phenol located on the electro-deficient sites of the carbon surface [20], thus covering an important part of the active sites. Consequently, only a small amount of them will be now available for hydrogen peroxide decomposition. On the other hand, the values of the exchange current (see i_o values in Table 3) significantly decreased compared to those of the corresponding starting materials. Those results evidence that phenol and hydrogen peroxide compete for the same active sites.

The exchange current value decreases from the fresh carbons to the pre-washed ones but their voltammograms maintain the same shape (Fig. 2) indicating that the redox cycle remains unchanged in the presence of phenol. Kinetic studies of hydrogen peroxide decomposition with the pre-washed carbon samples were carried out for the sake of confirming their cyclic voltammetry behavior. The values of the pseudo-first order rate constant (k_d) are collected in Table 3. The activity ranking derived from these values is in agreement with the predicted from the cyclic voltammetry results: AC-M > AC-P > w-AC-M > w-AC-P. The k_d and i_o values of the phenol pre-washed carbons can be also fitted to the linear correlation obtained for the fresh carbons (Fig. 4S, Supporting Information), which indicates that the activity of the available sites remain unaltered.

In conclusion, the accessibility of hydrogen peroxide to the active sites is hindered by the presence of phenol when relatively high concentrations (5 g/L in this case) are used and, consequently, the rate of hydrogen peroxide decomposition in CWPO will slow down.

3.3. Catalytic wet peroxide oxidation of phenol

The time-evolution of phenol, hydrogen peroxide and TOC conversions under the selected operating conditions (at hydrogen peroxide dose corresponding to the stoichiometric amount for

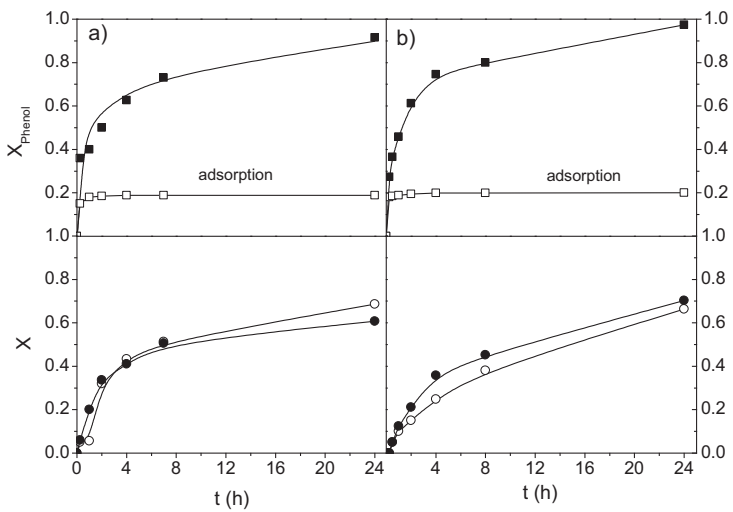

Fig. 3. Time-evolution of phenol (■), H_2O_2 (○) and TOC (●) conversions upon CWPO with AC-M (a) and AC-P (b). Operating conditions: $C_{Phenol,o} = 5$ g/L, $C_{H_2O_2,o} = 25$ g/L, $C_{cat} = 2.5$ g/L, $T = 80$ °C and pH_o 3.5.

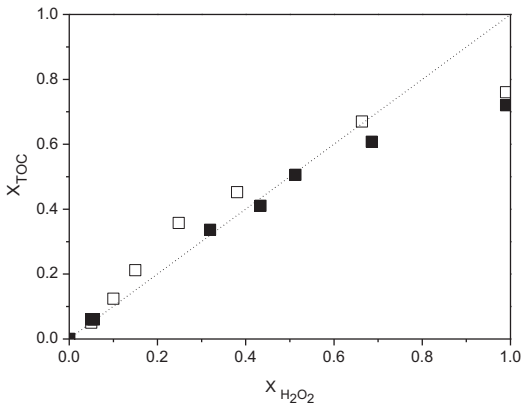

Fig. 4. TOC *vs* H_2O_2 conversions at the operating conditions of Fig. 3; (■) AC-M, (□) AC-P.

complete mineralization of phenol), are shown in Fig. 3. The concentration of Fe in the liquid effluent after 24 h reaction was 0.25 and 0.02 mg/L for AC-M and AC-P, respectively. Therefore, homogeneous contribution due to Fe in solution can be considered negligible. For the sake of discrimination between adsorption and reaction, the phenol adsorption curves obtained in the absence of hydrogen peroxide are also included. As observed, the adsorption capacity is similar for both carbons, about 20% of phenol being adsorbed under the operating conditions. Also, the adsorption kinetics were similar, since the same time was required to reach the equilibrium concentration with both carbons, around 30 min. Phenol conversions above 95% were achieved after 24 h reaction time, whereas around 20% was achieved in the absence of the activated carbons (Fig. S5 of Supporting Information). As expected, according to the higher content of ashes, AC-M exhibited higher initial activity for hydrogen peroxide decomposition than AC-P and therefore, a faster initial TOC reduction was observed with the former. However, somewhat higher phenol and TOC conversions were achieved with the second at the end of the 24 h-experiments.

TOC *vs* hydrogen peroxide conversion values are plotted in Fig. 4. As can be seen, 100% efficiency was maintained in the case of AC-M up to hydrogen peroxide conversion around 65% (24 h reaction). Beyond that value, further consumption of hydrogen peroxide was not associated to an equivalent TOC abatement, which remained around 70% even in a three-day experiment in spite of the fact that complete hydrogen peroxide decomposition was achieved. This is due to the refractoriness of some short-chain organic acids identified as oxidation by-products.

In the case of AC-P, TOC conversions were systematically higher than H_2O_2 conversions up to values of 50% $X_{H_2O_2}$. The only explanation found for these results is that part of the TOC is removed by adsorption of phenol and aromatic intermediates. AC-P, with a more developed mesoporous structure (Table 1), might benefit the reactant surface distribution resulting in a more favored adsorption. This adsorption contribution can also explain the aforementioned somewhat higher phenol conversions obtained with this catalyst compared to those for AC-M.

3.3.1. Oxidation route

The distribution of intermediates and by-products from CWPO of phenol with AC-P is shown in Fig. 5 in terms of equivalent carbon concentration. The same oxidation species and a similar distribution were obtained with AC-M (Fig. S6 of Supporting Information). The intermediates detected were aromatic compounds, such as catechol, resorcinol, hydroquinone and *p*-benzoquinone, and the by-products were low molecular weight organic acids, such as maleic, malonic, acetic, oxalic and formic. Both groups of reaction products were identified from the earliest stages of the process, which indicates that phenol can be either attacked by hydroxyl radicals in selective *meta*, *orto* or *para* positions, leading to the formation of catechol, resorcinol and hydroquinone, respectively (Fig. 5a), or simultaneously attacked by several hydroxyl radicals in different positions yielding carboxylic acids upon ring opening (Fig. 5b). The aromatic intermediates showed a maximum at around 1 h of reaction time and finally, were completely converted to carboxylic acids whose their residual concentration represented close to 25% of the initial phenol, in terms of carbon.

The TOC values calculated from the identified by-products were fairly close to the experimental TOC measurements (the time-profile evolution is provided in Fig. S7, Supporting Information). The color of the effluents turned from yellowish at short reaction times into colorless after 24 h reaction. Thus the presence of condensation by-products in the liquid effluent, typically detected in Fenton oxidation [21] can be considered negligible.

A remarkable benefit of the use of activated carbons in wet peroxide oxidation is the lower amount of highly ecotoxic by-products in comparison with the homogeneous oxidation process (blank experiment, Fig. S8, Supporting Information). In particular, the concentration of hydroquinone, the most ecotoxic species [22], was 7 times lower in catalytic than in homogeneous oxidation (Fig. S8). The aromatic intermediates were completely converted after 24 h of reaction in the case of CWPO, whereas concentrations up to 325 mg C/L of catechol were still remaining upon the same reaction time of homogeneous oxidation.

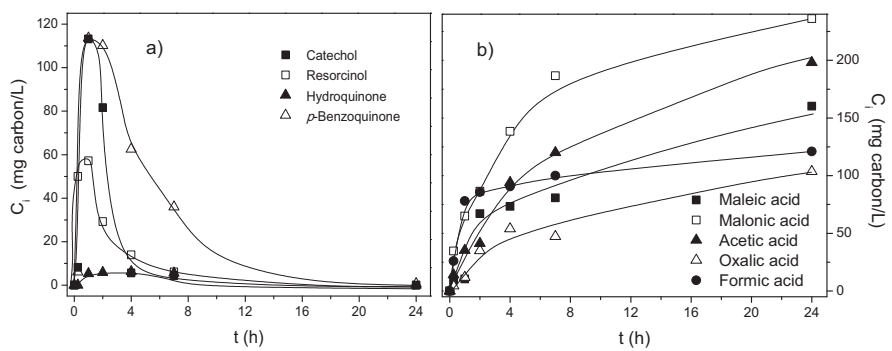

Fig. 5. Time-evolution of intermediates (a) and by-products (b) upon CWPO of phenol with AC-P at the operating conditions of Fig. 3.

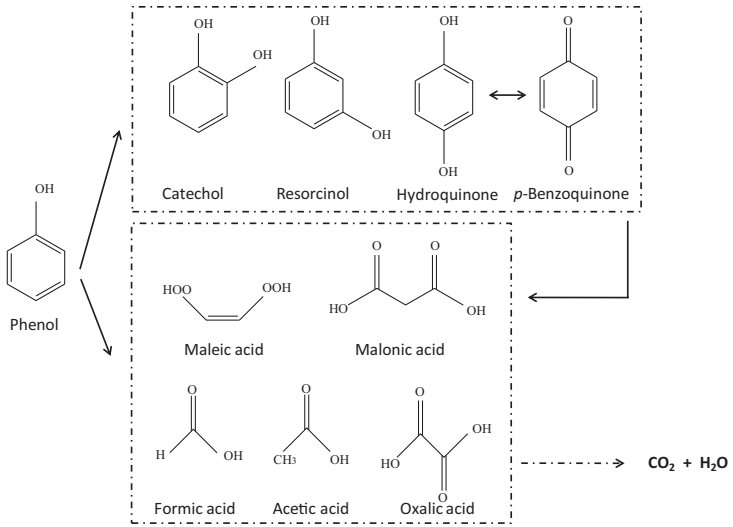

Fig. 6. Reaction pathway of CWPO of phenol with activated carbon.

From the concentration profiles of Fig. 5, the parallel-series reaction pathway of Fig. 6 is proposed. The carboxylic acids could be completely mineralized under appropriate operating conditions [23]. The fact that resorcinol was not detected in homogeneous wet peroxide oxidation, reveals that the oxidation of phenol in the presence of AC takes place simultaneously on the carbon surface, where hydroxyl and hydroperoxy radicals are formed, and in the liquid phase, where the radicals are released (as detected by the methylene blue dye test, Fig. S9, Supporting Information).

3.3.2. Catalyst stability and reusability

Four successive experiments of CWPO were carried out with AC-P. After each run, the carbon was separated by filtration and dried at 60 °C for 24 h without any further treatment. The phenol, TOC and hydrogen peroxide conversion values at 8 and 24 h reaction times in the different cycles (24 h each) are shown in Fig. 7a and b respectively. As can be seen, phenol and TOC abatement gradually decreased upon the successive runs consistently with the progressive decrease of hydrogen peroxide conversion. Noteworthy, the difference between the TOC and hydrogen peroxide conversion values at high reaction times seems to increase with the cycles (Fig. 7b). Apparently, the efficiency of hydrogen peroxide consumption tends to decrease.

The decreased ability of the activated carbon to decompose hydrogen peroxide was also evidenced by cyclic voltammetry. The initial coulombic charge of 1.37 mC measured for w-AC-P was reduced to 1.08 mC after the 4th use (Table 3). The reason is the reduction of the specific surface area [16] caused by the reaction species adsorbed or deposited on the carbon surface (see S_{BET} values of the w-AC-P and 4th use AC-P in Table 1). Consequently, the carbon active sites for hydrogen peroxide reduction, involved in hydroxyl radical formation, become unavailable upon CWPO. This fact is demonstrated by the 63% decrease in the exchange current (*cf.* i_o in Table 3, calculated from Fig. 8), which is the most important variable governing carbon activity [16].

The causes of the deactivation can be analyzed on the basis of the results from the characterization of the 4th use AC-P. The BET surface area and micropore volume significantly decreased with respect to the pre-washed carbon (Table 1), whereas the external area remained almost similar. Besides, the elemental analysis of the used carbon presents some significant differences with the fresh one (Table 2). These alterations can be attributed to the presence of

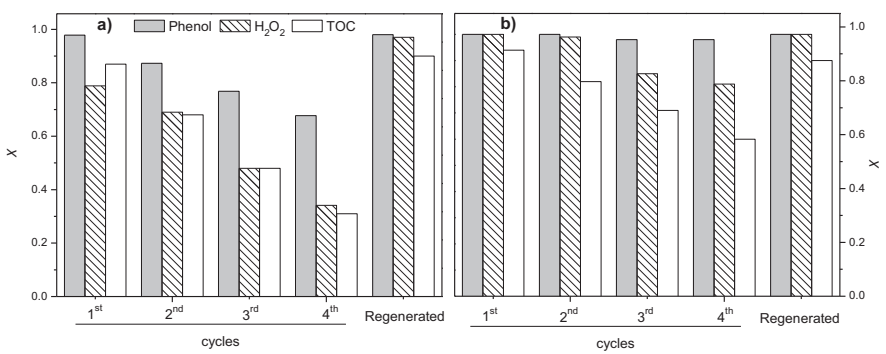

Fig. 7. Performance of AC-P in successive experiments at 8 h (a) and 24 h (b) reaction time: $C_{Phenol,o}$ = 1 g/L, $C_{H_2O_2,o}$ = 5 g/L, C_{cat} = 5 g/L, and pH_o 3.5.

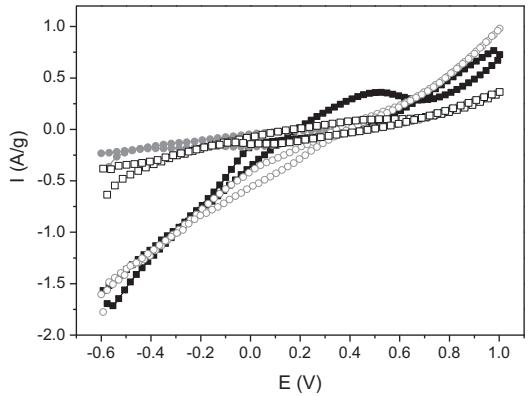

Fig. 8. Cyclic voltammograms of fresh and used AC-P in the presence of H_2O_2. Operating conditions: $C_{H_2O_2,o}$ = 25 g/L, v = 10 mV/s, 25 °C, pH 3.5 (HCl); (■) AC-P (□) w-AC-P, (●) 4th use AC-P, (◯) Reg. AC-P.

carbonaceous material (*i.e.* phenol, aromatic intermediates, condensation products) adsorbed on the carbon surface that block the access of N_2 to the micropores and would explain the relative decrease of C and the increase of H and O in the elemental analysis. In this sense, the amounts of CO_2 and CO evolved upon TPD up to 1100 °C (Table 1) from AC-P and 4th use AC-P (see Fig. S3 of Supporting Information for TPD profiles) show that CWPO dramatically affects the surface composition, the AC-P catalyst being strongly functionalized upon this treatment. Table 3 summarizes the assessment of the SOGs from the deconvolution of the TPD profiles. As can be observed, the amount of each type of group (carboxylic acid, lactone, anhydride from evolved CO_2 and anhydride, phenol, ether and carbonyl/quinone from CO) has increased, in particular, carboxylic acid, lactone and anhydride. In addition, CO_2 evolved from 600 to 800 °C revealed the presence of new groups such as pyrone.

TGA-DTG analysis of the fresh, pre-washed, and used (2nd and 4th use) AC-P carbon in air atmosphere was carried out and the results are depicted in Fig. 9. The pre-washed and used carbons, specially the 4th use, show higher weight-loss percentage than the fresh one due to the burn-off of adsorbed phenol and oxidation products. The DTG of the phenol-pre-washed carbon shows a smooth band centered around 200 °C which can be assigned to phenol burn-off whereas the 4th use carbon shows a clearly-seen peak at higher temperatures (350 °C) which can be assigned to the burn-off of condensation species adsorbed on the carbon surface. These are oligomers progressively formed upon the oxidation process since that peak scarcely appears in the 2nd use carbon. The oxidative coupling of phenol on the carbon surface stimulated by the presence of radicals has been already reported in the literature [24,25].

It is of practical interest to learn on the regeneration of the activated carbon. The regeneration of activated carbons affected by phenol-like oligomers has been studied by wet air oxidation at 150–240 °C and 0.2–1 MPa [26] and catalytic air oxidation at 240–300 °C in air [27]. In our case, we have checked a simple oxidative thermal regeneration at temperature somewhat higher than 300 °C according to the DTG but below that of AC burn-off (500 °C). The heating of the 4th use AC-P at 350 °C in air atmosphere (Hobersal, Model 10-PR/200 oven) during 24 h resulted in almost complete removal of the carbon deposits (see DTG of regenerated carbon in Fig. 9) with a fair recovery of the textural properties of the AC (see S_{BET}, A_{ext} and V_m in Table 1). The regeneration process provoked an important decrease of the most acidic SOGs, those decomposing at around 350 °C in the regeneration treatment. As seen in Table 4 (*cf.* 4th use and Reg. AC-P), carboxylic acid groups were depleted, while the amount of lactone and anhydride groups was significantly reduced. In addition, the regeneration in air atmosphere induced the creation of less acidic groups, such as phenol, ether and carbonyl/quinone (Table 4), which might be originated by the oxidation of the most acid groups. Then, the carbon surface does not recover its original chemical composition after the regeneration treatment (*cf.* fresh and Reg. AC-P in Table 4 and elemental analysis in Table 2). Carboxylic acid groups disappear, pyrone groups are now present and the rest of the SOGs are in significant higher amounts. These groups make up the chemical composition of the carbon surface since the carbonaceous deposits were mostly removed (see DTG of regenerated carbon in Fig. 9).

Cyclic voltammetry proved that in spite of the higher amount of SOGs of the regenerated AC-P compared to the fresh one, the electrochemical properties of the starting carbon were recovered (Fig. 8 and Table 3). The exchange current value was even slightly increased (0.156 A/g for Reg. AC-P *vs.* 0.147 for as-received AC-P), and consequently, the apparent kinetic constant for hydrogen peroxide decomposition was higher for the regenerated than for the fresh AC-P (Table 3). These results demonstrate that the accessibility of the carbon active sites has been restored as well as the catalyst performance (Fig. 7).

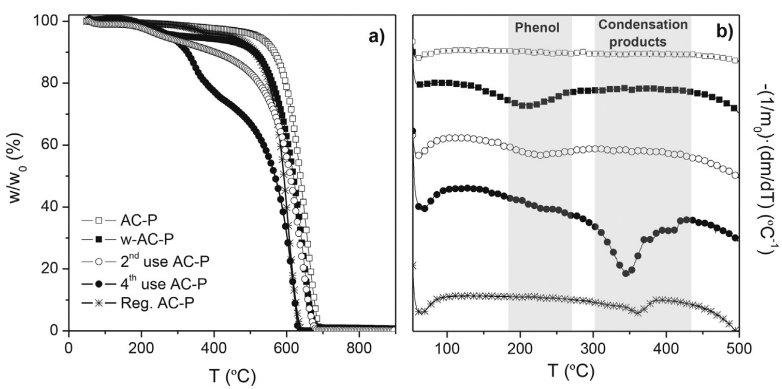

Fig. 9. TGA (a) and DTA (b) of fresh, spent and Reg. AC-P in air at 10 °C/min heating rate.

Table 4
Assessment of surface oxygen groups from deconvolution of TPD profiles for AC-P.

Sample	Groups evolved as CO_2 (μmol/g)				Groups evolved as CO (μmol/g)			
	Carboxylic	Anhydride	Lactone	Pyrone	Anhydride	Phenol	Ether	Carbonyl[a]
AC-P	59	50	22	0	34	119	278	299
4th use AC-P	646	469	154	88	315	967	897	385
Reg. AC-P	0	105	345	85	0	1673	2454	613

[a] Included carbonyl, quinone, chromene.

4. Conclusions

Activated carbons can act as efficient catalysts in the wet peroxide oxidation of phenolic wastewater if the operating conditions are adequate. Working under pollutant concentration and pollutant/carbon mass ratios higher than those commonly used in the literature so far allows avoiding or significantly reducing the non-effective consumption of hydrogen peroxide in parasitic reactions thus giving rise to improved efficiency (*i.e.* 97% phenol and 70% TOC conversions were achieved at 80 °C and 24 h with AC-P).

Under these operating conditions, great part of the carbon surface is occupied by phenol and the amount of active sites available is reduced. As a consequence, more controllable hydrogen peroxide decomposition into hydroxyl and hydroperoxy radicals takes place and these species efficiently react with phenol in the vicinity of the carbon surface, reducing parasitic recombination and allowing a more efficient consumption of hydrogen peroxide.

Phenol is oxidized in a parallel-series reaction pathway where all the intermediate products, aromatics such as catechol, resorcinol hydroquinone and *p*-benzoquinone, and by-products low molecular weight acids, such as maleic, malonic, acetic, oxalic and formic were successfully identified. Condensation by-products remained adsorbed on the carbon surface which represents an important advantage regarding to wastewater cleaning but provokes the progressive deactivation of these AC catalyst. Nevertheless, the activity can be recovered by simple oxidative thermal regeneration at 350 °C.

Acknowledgment

The authors wish to thank the Spanish MICINN for the financial support for the projects CTQ2008-03988/PPQ, CTQ2010-14807 and S2009/AMB-1588.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2013.04.068.

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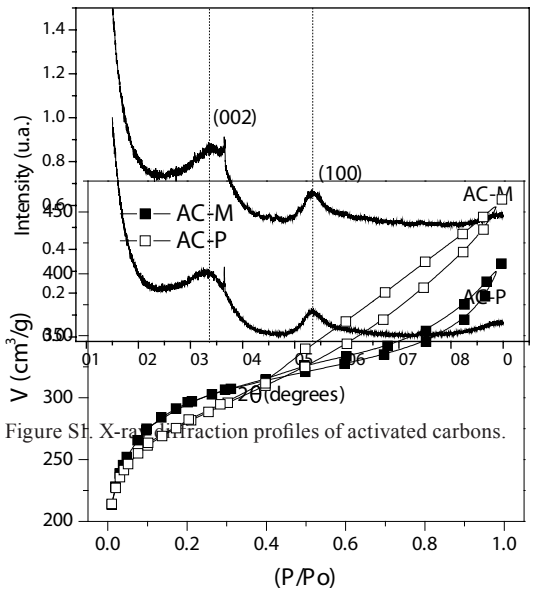


Figure S1. X-ray diffraction profiles of activated carbons.

Figure S2. 77 K N_2 adsorption/desorption isotherms of activated carbons.

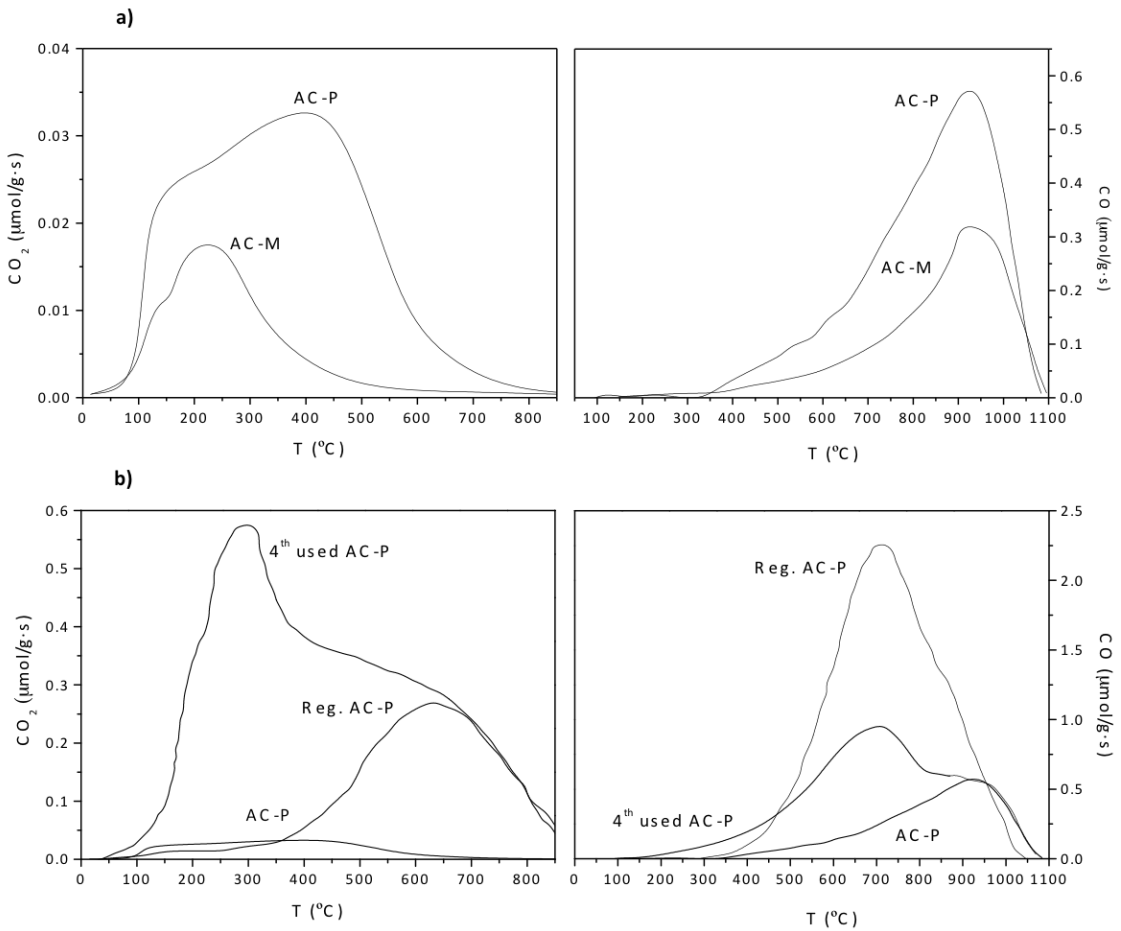


Figure S3. TPD profiles of activated carbons (a) and AC-P after different treatments (b).

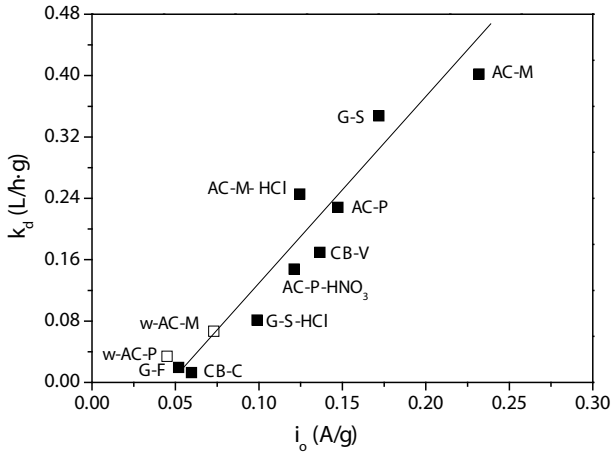


Figure S4. Relationship between the exchange current (i_o) and the apparent first-order rate constant (k_d) for hydrogen peroxide decomposition with different carbons materials. Close symbols: data from ref. 16, open symbols: data from w-AC-M and w-AC-P-w.

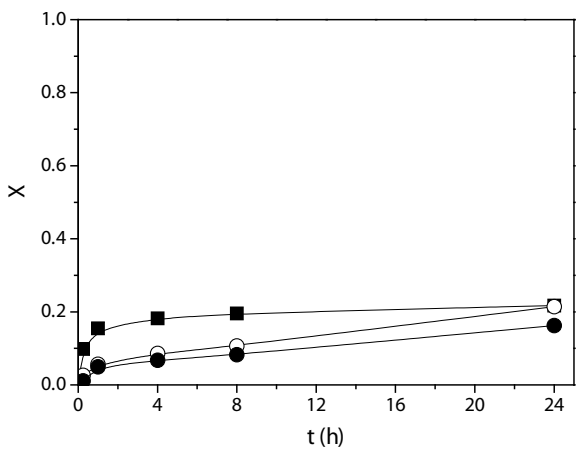


Figure S5. Time-evolution of phenol (■), H_2O_2 (○) and TOC (●) conversions upon CWPO in the absence of activated carbon. Operating conditions: $C_{Phenol,o}$=5 g/L, $C_{H2O2,o}$=25 g/L, T=80 ºC and pH_o=3.5.

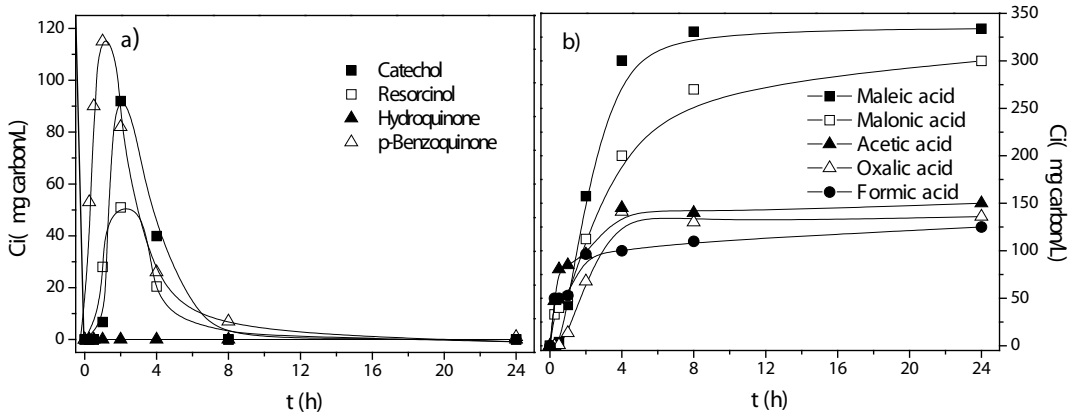


Figure S6. Time-evolution of intermediates (a) and by-products (b) upon CWPO of phenol with AC-M at the operating conditions of Figure 3.

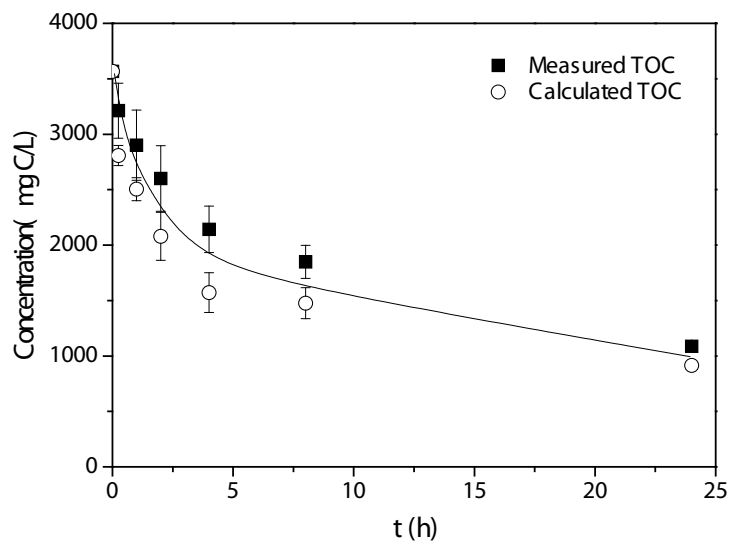


Figure S7. Time-evolution of measured and calculated TOC values upon CWPO of phenol with AC-P at the operating conditions of Figure 3.

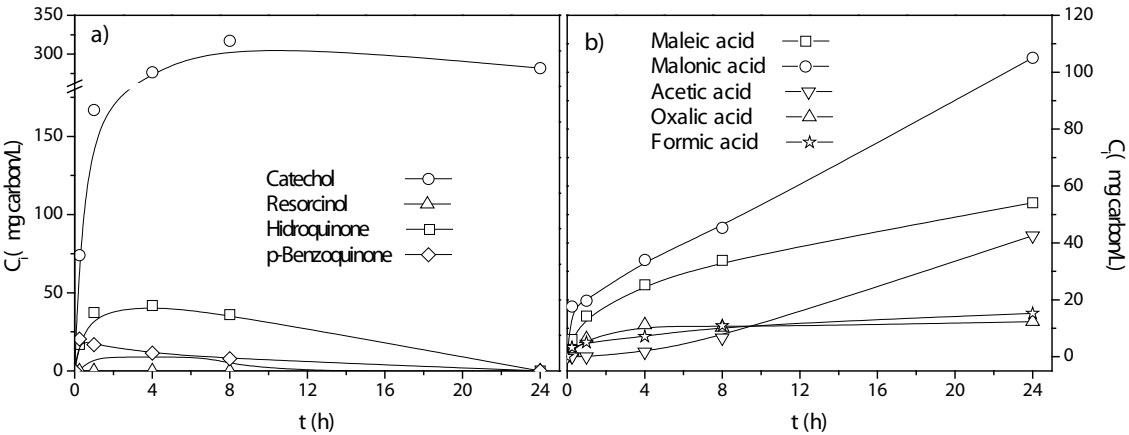


Figure S8. Time-evolution of intermediates (a) and by-products (b) upon homogeneous WPO of phenol (blank experiment). Operating conditions: $C_{Phenol,o}$=5 g/L, $C_{H2O2,o}$=25g/L, T=80 ºC and pH_o=3.5.

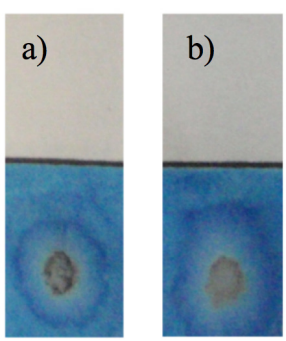
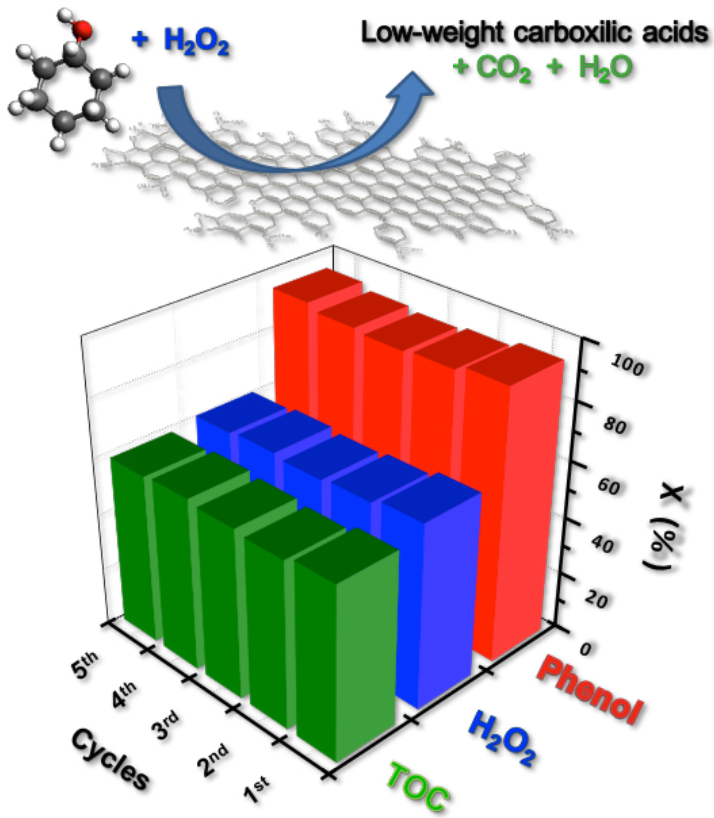


Figure S9. Detection of radicals in the liquid effluent from hydrogen peroxide decomposition in the presence of activated carbon by methylene blue method at 4 h reaction time. a) AC-M, b) AC-P.

Capítulo V. Graphite and carbon black materials as catalyst for wet peroxide oxidation



Applied Catalysis B: Environmental 144 (2014) 599–606

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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Graphite and carbon black materials as catalysts for wet peroxide oxidation

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ARTICLE INFO

Article history:
Received 12 June 2013
Received in revised form 26 July 2013
Accepted 30 July 2013
Available online xxx

Keywords:
Carbon black
Graphite
Hydrogen peroxide
Catalytic wet peroxide oxidation
Cyclic voltammetry

ABSTRACT

This study explores the application of non-porous carbon materials, two graphites (G-F, G-S) and two carbon blacks (CB-V and CB-C) as catalysts for wet peroxide oxidation (CWPO). The activity, efficiency and stability of these carbon materials have been evaluated using phenol as target compound. The catalyst screening experiments were carried out batch-wise at $C_{Phenol,0}$ = 1 g/L, $C_{H_2O_2,0}$ = 5 g/L, C_{cat} = 2.5 g/L, T = 80 °C and pH_0 = 3.5. The results allow concluding that CB-C was the most stable catalyst, although it showed a lower oxidation and mineralization activity than G-S and CB-V. Increasing the temperature up to 90 °C allowed complete phenol conversion and around 70% TOC reduction with 100% efficiency of hydrogen peroxide consumption upon 20 h reaction time at 5 g/L CB-C load. As a consequence of the initial oxidation of the carbon surface, the electrochemical properties of CB-C were favorably changed upon CWPO and its catalytic performance was improved from the first to the second use and then maintained upon successive applications in a five-cycle test.

1. Introduction

Catalytic wet peroxide oxidation (CWPO) relies on the oxidation of organic water pollutants with hydroxyl and hydroperoxyl radicals produced upon decomposition of hydrogen peroxide in the presence of a catalyst, typically iron, under working temperatures of 50–130 °C and pressures of 1–5 atm. Homogeneous CWPO technology has been commercialized under different proprietary processes, US Peroxide, OXY-PURE®, OHP® and PROX T.E.C [1]. These commercial systems are attractive because of their simple design and cost-effective operation. The disadvantages of homogeneous CWPO are the sensibility to pH, which must be always within the 2.5–3.5 range and the continuous loss of the dissolved iron catalyst which moreover needs to be separated from the effluent to avoid additional pollution. These issues have driven the investigation of active and stable solid catalysts, which has resulted in a growing literature on heterogeneous CWPO. A comprehensive survey of recent research on solid catalysts for CWPO is provided in the reviews of Perathoner and Centi [2], Garrido-Ramírez et al. [3], Navalon et al. [4] and Dhaskshinamoorthy et al. [5]. According to them, most CWPO studies are devoted to the incorporation of Fe, Mn, Co or Cu, as oxide species, metal complexes or in the form of nanoparticles on different supports, such as zeolites, mesostructured materials, silica, alumina, pillared clays and activated carbons. Some studies with supported noble metals such as Pt, Ru, Pd and Au, have been also recently published [1,6,7]. It must be highlighted the difficulty of comparing the results on the activity of the different catalysts since specific operating conditions, *i.e.* pH, pollutant/catalyst ratio, temperature, amount of hydrogen peroxide and the way of feeding it to the wastewater have been used.

The difficulty of developing suitable catalysts is noticed in the literature. Finding efficient and stable catalysts allowing detoxification of wastewater upon reasonable reaction times is an important challenge. Solid catalysts are usually unstable in the long term because of the leaching of the active phase as a consequence of the low pH caused by the presence of organic acids as by-products which also can give rise to the formation of metal complexes, particularly with oxalic acid [8,9].

The catalytic efficiency is associated to the selectivity for hydrogen peroxide decomposition into active hydroxyl and hydroperoxyl radicals, capable of breaking-down the organic pollutants instead of being consumed in un-productive (parasite) reactions. Efficient catalysts are desirable to provide the maximum TOC removal per unit of hydrogen peroxide, a crucial issue for the economy of the system. This concept is receiving increasing attention in the literature [10–13]. The interest for stable catalysts avoiding metal leaching has promoted the exploration of bare carbon materials, whose lower activity, compared to metal-bearing catalysts, can be

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http://dx.doi.org/10.1016/j.apcatb.2013.07.069

compensated by working at higher loads, which does not represent a drawback if they can be purchased at a lower cost. Activated carbons have been the most commonly used carbon materials in CWPO [4,8,14–22]. They exhibit donor-acceptor surface properties. The electron-rich sites such as basic surface oxygen groups and basal planes allow hydrogen peroxide decomposition into radical species through an electron transfer reaction similar to the Fenton mechanism [23]. Their efficiency for the decomposition of hydrogen peroxide is highly dependent on the adsorption of the organic pollutants, as recently demonstrated by Dominguez et al. [22]. In that work, unprecedented hydrogen peroxide efficiencies of almost 100% were reported for the CWPO of phenol with activated carbons. Under the selected reaction conditions (high pollutant concentration, 5 g/L of phenol and pollutant/carbon mass ratio = 2), great part of the carbon surface was occupied by phenol and the amount of available active sites was reduced. As a consequence, better controlled hydrogen peroxide decomposition into hydroxyl and hydroperoxy radicals was achieved and these species efficiently reacted with phenol in the vicinity of the carbon surface, reducing parasitic recombination and allowing a more efficient consumption of hydrogen peroxide. Catalyst stability was an important issue analyzed in that work. The activated carbon showed a progressive deactivation upon successive uses as a consequence of condensation by-products formed on the carbon surface. The activity was easily recovered by oxidative thermal regeneration (350 °C, 24 h).

In the current work, we explore the application of other carbon materials such as graphite and carbon black, of much lower surface area that can be available at reasonable low cost. The activity of these carbon materials for hydrogen peroxide decomposition was already demonstrated in a previous work [23]. The purpose of the present study is to evaluate their activity, efficiency and stability in CWPO using phenol as target compound. It is expected that with these materials of low adsorption capacity, deactivation by adsorbed condensation by-products can be avoided, or greatly reduced.

To the best of our knowledge, there are no previous studies on the application of carbon blacks for CWPO, whereas graphites have been scarcely studied in that process yielding in general fairly poor results [14,24].

2. Experimental

2.1. Reagents

Aqueous phenol solutions were prepared (1 g/L) (Sigma–Aldrich) at pH = 3.5 (HCl, Panreac). Hydrogen peroxide solution (30%, w/w) was purchased from Sigma–Aldrich. Working standard solutions of phenol, hydroquinone, resorcinol, catechol, *p*-benzoquinone, acetic acid, formic acid, malonic acid, maleic acid all from Sigma–Aldrich and oxalic acid (Panreac) were prepared and used for high performance liquid chromatography (HPLC) and ionic chromatography (IC) calibration. Other reagents used in the analyses were H_2SO_4 (Panreac), C_2H_3N (Riedel-deHaën), Na_2CO_3 (Panreac), $NaHCO_3$ (Merck), $Na_2S_2O_8$ (Panreac), HPO_4 (Fisher), $C_6H_4COOHCOOK$ (Aldrich), $TiOSO_4$ (Riedel-deHaën). All these reagents were of analytical grade and were used without further purification. All the solutions were prepared with milli-Q water.

2.2. Catalysts

Commercial graphites, supplied by Fluka (G-F, ref.: 1249167) and Sigma-Aldrich (G-S, ref.: 282863) and two carbon blacks, supplied by Chemviron (CB-C, ref.: 2156090) and Vulcan (CB-V, ref.: CC72R) were tested as catalysts for CWPO of phenol. All samples were provided in powder form.

2.3. Catalyst characterization

Structural characterization of the carbon materials by powder X-ray diffraction (XRD) was carried out in a Siemens Model D5000 X-ray diffractometer, using Cu Kα (8.04 keV) radiation and a step of 0.02°/s for $2\theta = 5-100°$ and analyzed with PDF 2000 (JCPDS-ICDD) software.

The specific surface area (S_{BET}) values were obtained from the N_2 adsorption/desorption isotherms at 77 K using a Micromeritics Tristar apparatus on samples previously outgassed overnight at 150 °C to a reduced pressure $<10^{-3}$ Torr in order to ensure a dry clean surface. The external or non-microporous surface area (A_{ext}) was calculated by the *t*-method. Elemental analyses were performed in a LECO Model CHNS-932 analyzer. Element identification in the carbon ashes was carried out by TXRF (Extra-II Rich & Seifert spectrometer). The amount of surface oxygen groups (SOG) in the carbons was accomplished by Temperature-programmed desorption (TPD) under N_2 (1000 NmL/min) as carrier gas. A carbon sample of 100 mg was placed in a quartz tube and heated at 10 °C/min from room temperature up to 900 °C. The evolved CO_2 and CO were measured by a SIEMENS gas analyzer (mod. Ultramat 22). Peaks deconvolution of the TPD spectra were adjusted to multiple Gaussian function by Peakfit 4.12 software.

Thermal gravimetric analyses (TGA) were performed on a Mettler–Toledo TGA/SDTA 851^e thermobalance in air atmosphere from 50 to 900 °C (10 °C/min).

Cyclic voltammetry (CV) measurements were carried out in a conventional three-electrode electrochemical cell, using a computerized potentiostat (Autolab PGSTAT 302, Eco Chemie). A glassy carbon electrode was used as substrate for the carbon samples, a gold electrode as the counter, a saturated Ag/AgCl, KCl electrode as the reference and HCl solution (pH = 3.5) as electrolyte. 20 μL of the carbon suspension (6 mg of carbon in 730 μL Milli-Q water) was dropped on the glassy carbon electrode to obtain a uniform film and subjected to CV (10 mV/s) under nitrogen atmosphere in the absence and presence of hydrogen peroxide (25 g/L) in the potential range from −0.6 to 1 V. From these measurements, the coulombic charge (CC) and the exchange current (i_o) were calculated. More detailed description of these tests has been reported elsewhere [23].

2.4. CWPO experiments

The CWPO runs were carried out batch-wise in a magnetically stirred three-necked glass reactor equipped with a reflux condenser. In a typical experiment, 45 mL of phenol solution (1 g/L) at pH = 3.5 (HCl) were placed in the reactor, along with the selected mass of carbon (0–0.375 g) and heated up to the desired temperature (80–90 °C). After that, 5 mL of an adjusted concentration of hydrogen peroxide aqueous solution were added and the stirring at 1200 rpm started. Effluents at different reaction times were taken from the reactor and immediately analyzed. After 24 h of reaction, the heating was switched-off and the reactor cooled to room temperature in cold water. Then, the catalyst was separated by filtration (0.45 μm Nylon filter) and dried at 60 °C. A blank experiment was carried out to assess the homogenous contribution. Phenol adsorption runs were performed at the same operating conditions as the oxidation tests but without hydrogen peroxide addition. The initial pH was set at 3.5 which is within the range most commonly reported in the literature for CWPO with iron catalysts [2]. All the experiments were performed by triplicate being the standard deviation always less than 5%.

Table 1
Structural and textural characterization and phenol adsorption of graphites and carbon blacks.

Sample	d_{002} (nm)	L_c (nm)	L_a (nm)	S_{BET} (m^2/g)	A_{ext} (m^2/g)	mg Ph/g C
G-F	0.337	46.63	48.87	6	6	6.44
G-S	0.338	44.09	48.70	12	12	13.88
CB-C (fresh)	0.348	7.08	6.57	75	67	27.20
Used CB-C	–	–	–	53[a]	49[a]	–
CB-V (fresh)	0.362	3.87	3.89	233	110	152.6
Used CB-V[b]	–	–	–	115	111	–

[a] 1st use after 24 h reaction.
[b] 4th use after 24 h reaction.

2.5. Analytical methods

Phenol and aromatic intermediates were identified and quantified by means of HPLC (Varian, Mod. ProStar) by a Nucleosil C18 5 mm column (Microsob-MV, 15 cm length, 4.6 mm diameter) using a mixture of 4 mM H_2SO_4 aqueous solution at 1 mL/min as mobile phase. A diode array detector (PDA detector) at wavelengths of 210 and 246 nm was used. Short-chain organic acids were determined by IC (Metrohm, mod. 883 BASIC IC Plus) with anionic chemical suppression using a conductivity detector. A Metrosep A supp 5-250 column (25 cm length, 4 mm diameter) was used as stationary phase and 0.7 mL/min of an aqueous solution 3.2 mM of Na_2CO_3 and 1 mM of $NaHCO_3$ as mobile phase. Total organic carbon was measured with a TOC analyzer (Shimadzu TOC V_{SCH}). Hydrogen peroxide concentration and iron in solution were determined by colorimetric titration with a UV 2100 Shimadzu UV-VIS spectrophotometer using the titanium sulfate [25] and *o*-phenantroline [26] methods, respectively.

3. Results and discussion

3.1. Catalyst characterization

The structural and textural characteristics of the graphites (G-S and G-F) and carbon blacks (CB-C and CB-V) are summarized in Table 1. The XRD profiles and N_2 adsorption-desorption isotherms of the four carbon materials tested along with the pore distribution of the carbon blacks are included as Supporting Information (Figures S1, S2 and S3, respectively). The C percentage from elemental analysis and the ash content along with the results from TPD are collected in Table 2.

As expected, the graphitic carbons show significantly higher structural order than the carbon blacks with much more developed crystalline domains as can be seen from the height (L_c) and width (L_a) dimensions calculated from the XRD profiles. The interlayer spacing value (d_{002}) of the two graphites is very close to the standard value (0.335 nm). Both graphites yielded very similar values of the crystalline structural parameters whereas some significant differences can be observed between the two carbon blacks.

Table 2
Elemental *C* (%, d.a.f.), ash content (%, d.b.) and surface oxygen groups of the carbon materials tested.

Sample	*C* (%)	Ashes (%)	CO_2 (μmol/g)	CO (μmol/g)
G-F	96.6	0.2	128	79
G-S	97.2	0.5	105	36
CB-C	≈99	0.0	83	214
1st use CB-C	98.4	0.0	197[a]/201[b]	226[a]/256[b]
CB-V	97.1	0.85	148	137
1st use CB-V	92.9	0.85	413	729

d.a.f., dry-ash-free basis; d.b., dry bases.
[a] 1st use after 24 h reaction.
[b] 4th use after 24 h reaction.

The graphites showed fairly low values of BET surface area (Table 1). This was also the case of CB-C carbon black, although with significantly higher specific area and some developed porosity due to the presence of narrow mesopores. Meanwhile, the CB-V carbon black, with substantially higher BET surface area, presents an important contribution of microporosity as well as narrow mesopores.

As expected, the chemical composition of these materials consists essentially of C (Table 2). Some low amounts of O are accompanying as surface oxygen groups (SOGs) (Table 2). The graphites contain majorly acidic CO_2-evolving SOGs whereas CB-C mostly presents CO-evolving SOGs. CB-V, with fairly similar amount of SOG as CB-C, contains both types of SOGs in about the same proportion (more detailed SOGs assessment is given in Table S1 of Supporting Information). The ash content was very low in all cases and almost negligible for CB-C (Table 2). Noteworthy, iron, the most critical ash constituent regarding CWPO, due to its widely demonstrated catalytic activity, was only present in G-S. According to TXRF analyses, this material contains 0.4 wt% of Fe. The non-negligible ash content in CB-V sample (0.85%, Table 2) is constituted mainly by Al, inert metal in CWPO processes.

The adsorption of phenol was checked (1 g/L phenol was stirred with 2.5 g/L carbon at 80 °C during 4 h), and the values are included in Table 1. As can be seen, the adsorption values vary consistently with the specific area being much higher for the CB-V carbon black. As indicated before, it would be desirable to use carbon materials with low phenol adsorption capacity with the aim of minimizing or even avoiding the formation of condensation products on the surface, which provokes deactivation [22]. Taking the reference of Panreac activated carbon (#:121237), which adsorbs 200 mg of phenol per gram of carbon under the same conditions, all the carbon materials tested in this study, except CB-V, yielded much lower adsorption.

3.2. Catalyst activity

The conversions of phenol, TOC and hydrogen peroxide achieved with each carbon upon CWPO after 4 h reaction time are given in Fig. 1. The removal of phenol achieved in the absence of hydrogen peroxide has been also included for the sake of discrimination between adsorption and reaction. Except in the case of CB-V, the contribution of adsorption is of very low significance, especially for graphites. As observed, all the carbon materials tested promoted the decomposition of hydrogen peroxide, showing different catalytic activity, which in terms of phenol conversion and partial mineralization follows the order: G-S > CB-V > CB-C > G-F.

The much higher catalytic activity of graphite G-S *versus* G-F in spite of their quite similar characteristics can be explained by the iron content of the former (0.4 wt%). In addition, 1.5 mg/L of Fe were detected in the liquid phase after 4 h reaction time with this graphite so that the homogeneous contribution of iron leached should not be discarded. To check this issue, a control experiment was carried out by removing the graphite after 1 h of reaction and continuing the reaction with the filtrate (where the leached Fe was

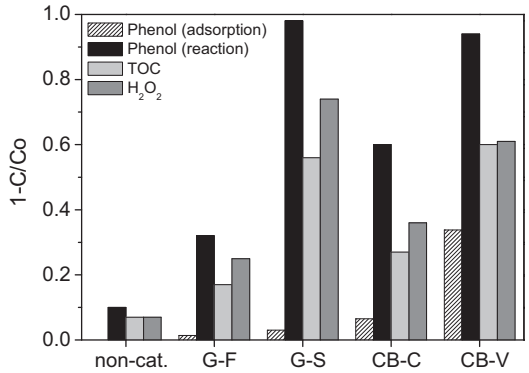

Fig. 1. Phenol disappearance (by adsorption and reaction), TOC removal and H_2O_2 decomposition after 4 h of reaction. Operating conditions: $C_{Phenol,0}$ = 1 g/L, $C_{H_2O_2,0}$ = 5 g/L, C_{cat} = 2.5 g/L, T = 80 °C and pH_0 = 3.5.

dissolved), during another 3 h. Eventually, similar phenol and TOC conversions as those obtained in presence of the G-S (Fig. 1) were observed, allowing to conclude that the activity observed with this catalyst is predominately due to the Fe leached.

With regard to carbon blacks, none of them contain Fe neither other active metallic ashes, and therefore, the carbon structure (electron-rich sites such as basic surface oxygen groups and basal planes) is the only responsible of the activity. As can be seen, CB-V showed a higher activity (*ca.* 93% phenol, 60% TOC and 60% hydrogen peroxide conversions) than CB-C due to its higher specific surface area which implies a higher amount of active sites for hydrogen peroxide decomposition [23].

3.3. Catalyst efficiency

The time-evolution of TOC removal and hydrogen peroxide consumption with the tested materials are given in Fig. 2. The mineralization curves follow a trend consistent with that of the hydrogen peroxide, the TOC disappearance being faster during the first 4 h of reaction, when phenol and aromatic intermediates breakdown to low-weight carboxylic acids and CO_2. In the case of CB-V, the TOC removal values at reaction times below 4 h are higher than those of H_2O_2 decomposition, which can be explained only by considering the adsorption contribution.

The efficiency of hydrogen peroxide, calculated as $X_{TOC}/X_{H_2O_2}$ [11], upon reaction time is depicted in Fig. 3. As observed, that efficiency increased with reaction time up to asymptotic values (90% for graphites and 100% for carbon blacks). In the early stages, the decomposition of hydrogen peroxide catalyzed by the carbon surface leads to high concentrations of hydroxyl radicals that favor parasite scavenging reactions. As hydrogen peroxide is consumed and the aromatic intermediates oxidized (visualized by the color change of the samples from brownish to colorless), the surface concentration of radical species decreases and the parasitic recombination is progressively reduced thus increasing the efficiency of H_2O_2 toward oxidation and eventually mineralization. The hydrogen peroxide efficiency at short reaction times can be improved by optimizing the operating conditions, as will be later demonstrated for the CB-C catalyst.

3.4. Catalyst stability and reusability

The most active carbon materials, *viz.* G-S, CB-V and CB-C, were tested in successive CWPO runs in order to analyze their stability.

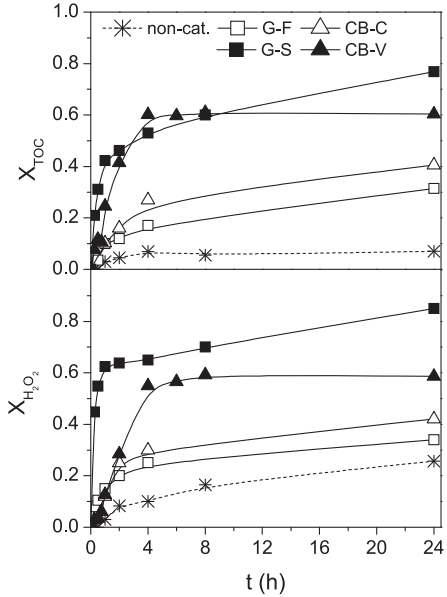

Fig. 2. TOC and H_2O_2 conversion profiles at the operating conditions of Fig. 1.

G-F was discarded for further studies because of its low activity in CWPO of phenol (Fig. 1). In each cycle, the catalyst was used during 24 h in reaction, then separated by filtration and dried at 60 °C for another 24 h before being used again in a new cycle. The phenol, TOC and hydrogen peroxide conversion values at 4 and 24 h reaction time upon successive cycles are given in Fig. 4a and b. The initial activity of G-S and CB-V decreased upon successive cycles, in particular for CB-V (Fig. 4a), though at higher phenol conversions that effect was significantly attenuated (Fig. 4b), those carbons recovered in part their performance and the differences with the more stable CB-C became much lower. In the case of G-S, the content of Fe was reduced by 15% from the first to the second use (due to leaching) and no further loss of Fe was detected in successive cycles. As indicated before, the activity of this carbon must be greatly

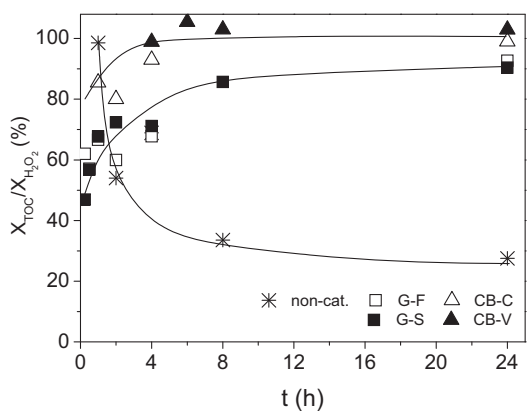

Fig. 3. Evolution of the efficiency of hydrogen peroxide consumption upon reaction time at the operating conditions of Fig. 1.

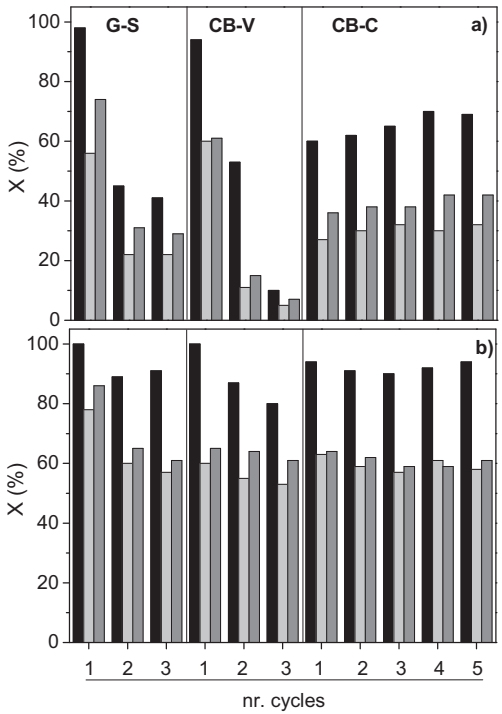

Fig. 4. Performance of the catalyst upon successive uses at 4 h (a) and 24 h (b) reaction time (X_{Phenol} ■, X_{TOC} □ and $X_{H_2O_2}$ ▩). Operating conditions: $C_{Phenol,0}$ = 1 g/L, $C_{H_2O_2,0}$ = 5 g/L, C_{cat} = 2.5 g/L (G-S, CB-V) and 5 g/L (CB-C), T = 80 °C and pH_0 = 3.5.

associated to the presence of iron as a main ash-component. Therefore, the decrease of iron content from the first to the second cycle and the absence of iron leaching (homogeneous contribution) in that second cycle can explain the decrease of the catalytic activity occurring only upon the two first uses.

The CB-V carbon black suffered almost complete deactivation after its second use (similar results were obtained in the third use of this catalyst and in the blank experiment at a reaction time of 4 h, *cf.* Figs. 1 and 4a) but a significant recovery of activity was observed at higher reaction time (Fig. 4b) although with a monotonical decay upon successive cycles. Important changes were observed in this carbon black after its use in CWPO experiments (see Table 1). The BET surface area was reduced up to the value of the external area which remained unaltered, thus indicating almost complete blockage of the micropores, confirmed from pore size distribution (see Figure S3 of Supporting Information). Besides, the elemental analysis of the used carbon showed a significant reduction of C compared to the fresh one (see Table 2). These changes can be attributed to the presence of organic species, most probably oligomers from oxidative coupling reactions, on the carbon surface. The TPD results (Table 1) serve also to support this conclusion. As observed, the amounts of CO and CO_2 evolved upon TPD are substantially higher in the used catalyst than in the fresh one. The deconvolution of the TPD profiles and the assessment of the SOGs from those profiles are provided in the Supporting Information (Figure S4 and Table S1, respectively). As can be observed, CO_2 evolved mainly from carboxylic acid groups and CO from phenol and ether groups created upon CWPO.

TGA-DTG analyses of the fresh and used (3rd cycle) CB-V carbon black in air atmosphere are depicted in Fig. 5, where it can be observed a higher weight-loss percentage of the used CB-V (Fig. 5a) due to the burn-off of adsorbed species. The DTG profile after the 3rd cycle clearly shows a peak somewhat above 300 °C (Fig. 5b). Formation of oligomeric condensation by-products on the carbon surface has been reported in a previous work on CWPO of phenol with activated carbons under similar operating conditions [22].

The CB-C carbon black showed no deactivation upon five successive cycles, where phenol conversion and TOC removal remained almost invariable. The efficiency of hydrogen peroxide consumption ($X_{TOC}/X_{H_2O_2}$) was maintained around 90% at the reaction times of Fig. 4. This suggests the absence of carbonaceous material adsorbed on the carbon surface, consistently with its low adsorption capacity. The TGA analyses confirmed this fact since similar weight-loss profiles were obtained for the fresh and 4th cycle CB-C (Fig. 5a) and the corresponding DTG curves did not show any peak (Fig. 5b).

Intriguingly, the initial performance of CB-C (Fig. 4a) showed a slight but monotonical improvement upon at least the first three cycles. The initial rate values depicted in Fig. 6 show a significant increase from the first to the second use of this carbon which then remained almost constant upon successive cycles. This initial

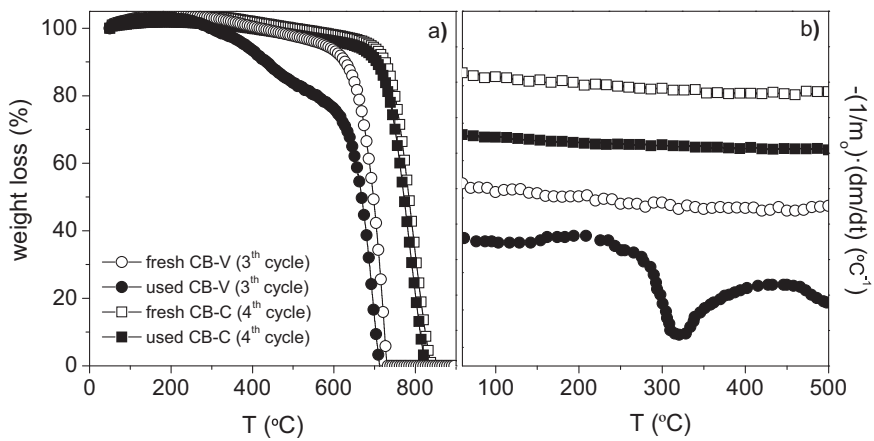

Fig. 5. TGA (a) and DTG (b) curves of fresh and used CB-V (3rd cycle), and fresh and used CB-C (4th cycle) in air at 10 °C/min heating rate.

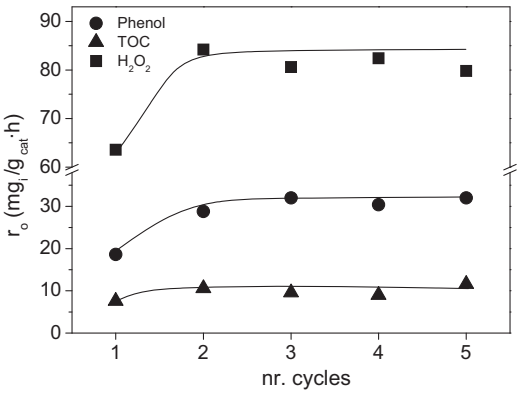

Fig. 6. Initial rates of phenol disappearance and TOC removal and hydrogen peroxide decomposition in sequential experiments over CB-C. Operating conditions: $C_{Phenol,0}$ = 1 g/L, $C_{H_2O_2,0}$ = 5 g/L, C_{cat} = 5 g/L, T = 80 °C and pH_0 = 3.5. Initial rates calculated as $(r_o)_i = (-dC_i/dt)_o/C_{cat}$.

increase is remarkably pronounced regarding to hydrogen peroxide decomposition.

To learn more on these results, cyclic voltammetry measurements of the fresh and used (2nd cycle) CB-C carbon black were carried out. The voltammograms obtained are presented in Fig. 7. The values of the coulombic charge (CC), calculated from Fig. 7a, and those of the exchange current (i_o), calculated from Fig. 7b, were 0.887 mC and 0.060 A/g, respectively, for the fresh carbon and 1.030 mC and 0.127 A/g for the used one. The evolution of the CC values indicates that the electrochemical capacity of CB-C increases upon its use in CWPO. The ability of CB-C to decompose hydrogen peroxide is enhanced after its use according to the increase of the i_o value. In addition, the background voltammogram of the used CB-C shows two signals that were not present in the fresh carbon (Fig. 7a). The first signal occurs when the applied potential goes to positive direction, in the range from 0.1 to 0.3 V, while the second one appears when the potential goes to negative direction, from 0.3 to 0 V. Both signals, only present in the used carbon, can be attributed to the oxidation and reduction of SOGs, respectively. The creation of some SOGs upon CWPO is confirmed by the TPD analyses and seems to occur only in the early stages, likely due to the initial exposition to hydrogen peroxide. The amounts of CO_2 evolved after the first use is significantly higher than from the fresh carbon and then remained almost constant (see Table 1). The SOGs formed are carboxylic acid and, in less extent, anhydride, ether and phenol (see Figure S3 and Table S1 of Supporting Information). The creation particularly of carboxylic acid groups confers some hydrophilic character to CB-C which was visualized by a better wettability of the solid when put in contact with aqueous phenol solution. This can favor the diffusion of the reagents to the active sites [27,28] and contribute to increase the carbon exchange current, enhancing the initial catalytic activity.

3.5. CWPO of phenol with CB-C

The preceding results support the potential application of the CB-C carbon black as a promising catalyst in CWPO. To learn more on its practical application, batch-wise experiments at different carbon loads, temperature and initial pH were performed.

Fig. 8 shows the time-evolution of phenol conversion and TOC removal at different catalyst loads (from 0 to 7.5 g/L), two temperatures (80 and 90 °C) and two initial pHs (3.5 and 6), always working at 1 g/L starting phenol concentration and the stoichiometric amount of hydrogen peroxide for complete mineralization. The positive effect of temperature can be clearly seen. Complete conversion of phenol was achieved at 90 °C but it required high catalyst load (5 g/L) and reaction times (around 20 h). Under these conditions, more than 70% mineralization was achieved. The remaining by-products were carboxylic acids, as can be seen in Fig. 9a. The highly toxic aromatic intermediates were completely converted upon 16 h reaction time. The values of TOC calculated from the species identified were always fairly close to the experimental TOC measurements (see Figure S5 of Supporting Information).

The efficiency of hydrogen peroxide consumption under the selected operating conditions of Fig. 8, is given in Fig. 10 where TOC removal *versus* H_2O_2 decomposition is depicted. The CB-C carbon allows a highly efficient consumption of hydrogen peroxide which is favored by increasing the temperature and the catalyst load. Therefore, these two issues enhance the selectivity toward oxidation inhibiting parasite scavenging reactions.

To check the influence of the initial pH, an experiment was performed at pH_o = 6, T = 80 °C and C_{cat} = 5 g/L. The evolution of phenol and TOC conversions with reaction time is depicted in Fig. 8, while the hydrogen peroxide efficiency values achieved at these conditions are included in Fig. 10. As can be seen, phenol and TOC conversions were somewhat lower at pH = 6 at the beginning of the reaction, but similar results as those obtained at pH = 3.5

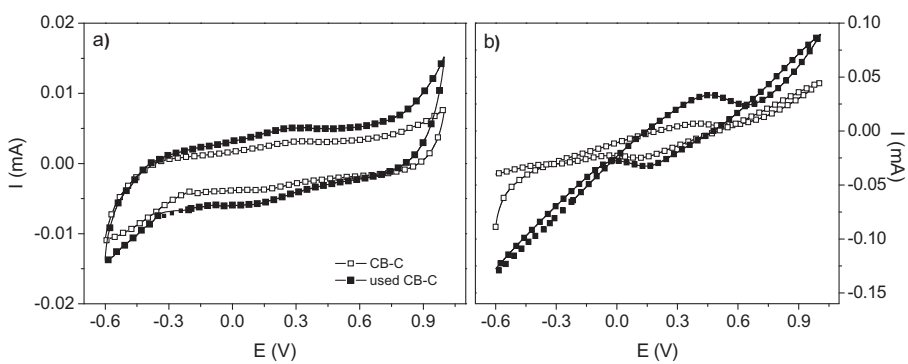

Fig. 7. Cyclic voltammograms of fresh and used CB-C in the absence (a) and the presence (b) of hydrogen peroxide. Operating conditions: v = 10 mV/s, T = 25 °C, pH = 3.5 (HCl), $C_{H_2O_2}$ = 25 g/L.

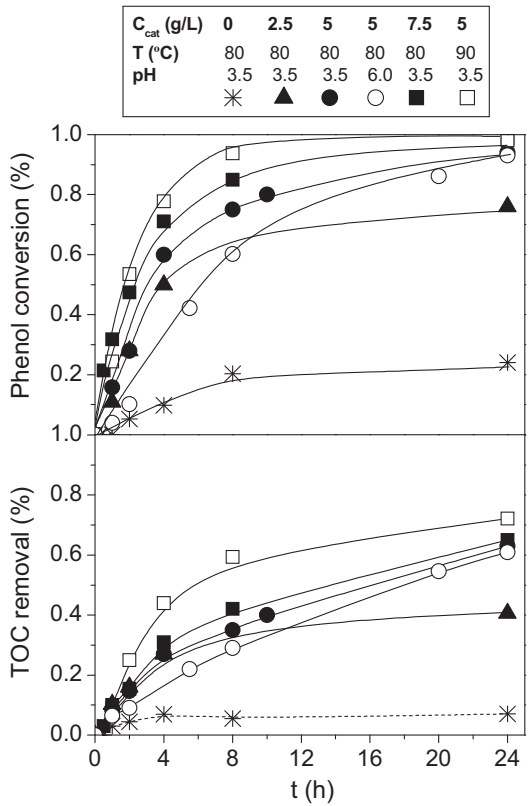

Fig. 8. Evolution of phenol and TOC upon reaction time in CWPO with the CB-C catalyst. Operating conditions: $C_{Phenol,0}$ = 1 g/L, $C_{H_2O,0}$ = 5 g/L.

were achieved after 24 h. The hydrogen peroxide efficiency was maintained around 100%. Therefore, in this case, the pH is not a so critical variable as commonly reported for iron-catalyzed wet peroxide oxidation. This represents an important advantage when near-neutral effluents are treated since avoids pH adjusting.

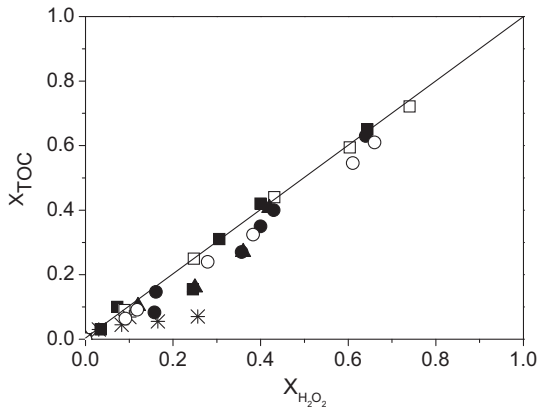

Fig. 10. TOC *versus* H_2O_2 conversions in CWPO of phenol with the CB-C catalyst at the operating conditions of Fig. 8 (symbols in Fig. 8).

4. Conclusions

Non-porous carbon materials with moderate specific area and without mineral impurities are efficient and stable catalysts for CWPO, as has been demonstrated by CB-C carbon black. This material presents sufficient electrochemical capacity to enable surface decomposition of hydrogen peroxide along with a low adsorption capacity to avoid or minimize the formation of adsorbed oligomeric by-products. Upon the early stages of the reaction, CB-C carbon black was oxidized resulting in an increased hydrophilic character which favored the diffusion of the reagents to the active sites, fact that contributed to increase the carbon exchange current, and therefore, its initial catalytic activity from its first to second use.

Complete conversion of phenol and around 70% TOC removal with 100% efficiency of hydrogen peroxide consumption were achieved in 20 h reaction time at moderate temperature (90 °C) with high catalyst load (5 g/L) at 1 g/L starting phenol concentration and the hydrogen peroxide dose corresponding to the stoichiometric amount for phenol complete mineralization within the range of initial pH tested (3.5–6). The final by-products are low-weight carboxylic acids, of much lower ecotoxicity than the starting phenol and the aromatic oxidation intermediates.

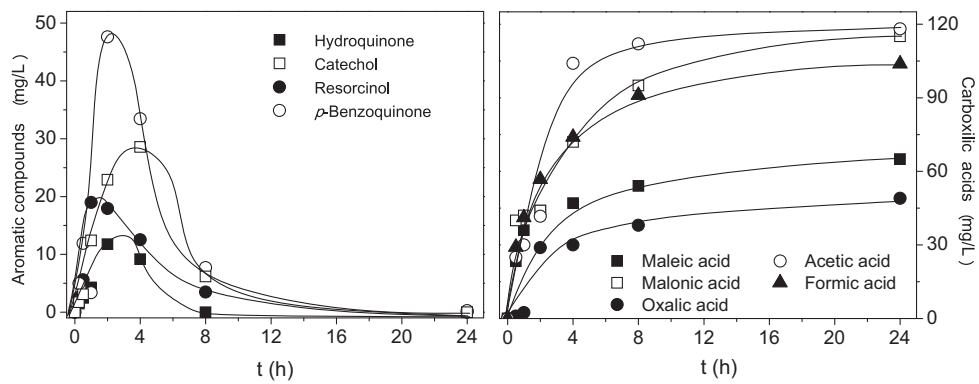

Fig. 9. Evolution of intermediates (a) and by-products (b) in CWPO of phenol with CB-C. Operating conditions: $C_{Phenol,0}$ = 1 g/L, $C_{H_2O,0}$ = 5 g/L, C_{cat} = 2.5 g/L, T = 90 °C and pH_0 = 3.5.

Acknowledgments

The authors wish to thank the Spanish MICINN for the financial support through the projects CTQ2008-03988/PPQ and CTQ2010-14807. The Comunidad Autónoma de Madrid is also gratefully acknowledged for the financial support through the project S2009/AMB-1588.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2013.07.069.

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Table S1. Assessment of surface oxygen groups from deconvolution of the TPD profiles of the fresh and used carbon blacks.

Sample	Groups evolved as CO_2 (μmol/g)				Groups evolved as CO (μmol/g)			
	carboxylic	anhydride	lactone	pyrone	anhydride	phenol	ether	carbonyl[a]
CB-C	23	7	14	38	4	26	-	193
1st use	128	40	20	8	24	96	24	80
4th use	113	43	32	13	28	75	49	103
CB-V	29	64	18	37	-	13	23	103
3th use	318	72	21	-	30	134	429	136

[a]includes carbonyl, quinone, chromene

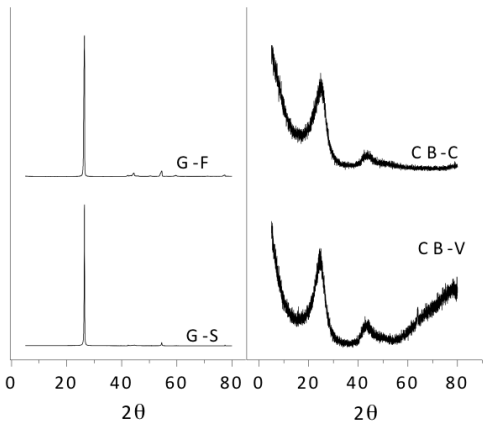


Figure S1. X-ray diffraction profiles of the carbon materials.

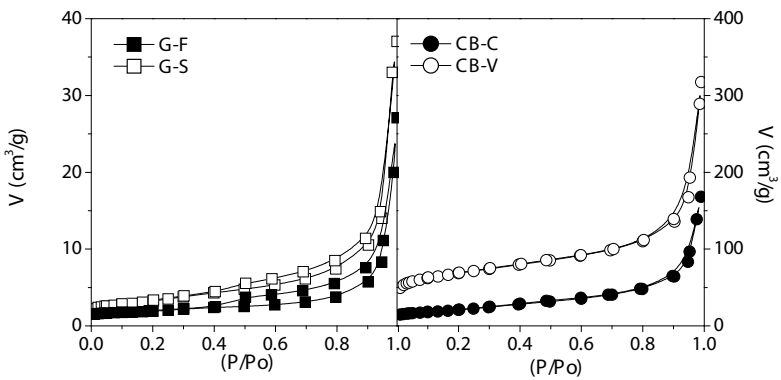


Figure S2. 77 K N2 adsorption/desorption isotherms of the carbon materials.

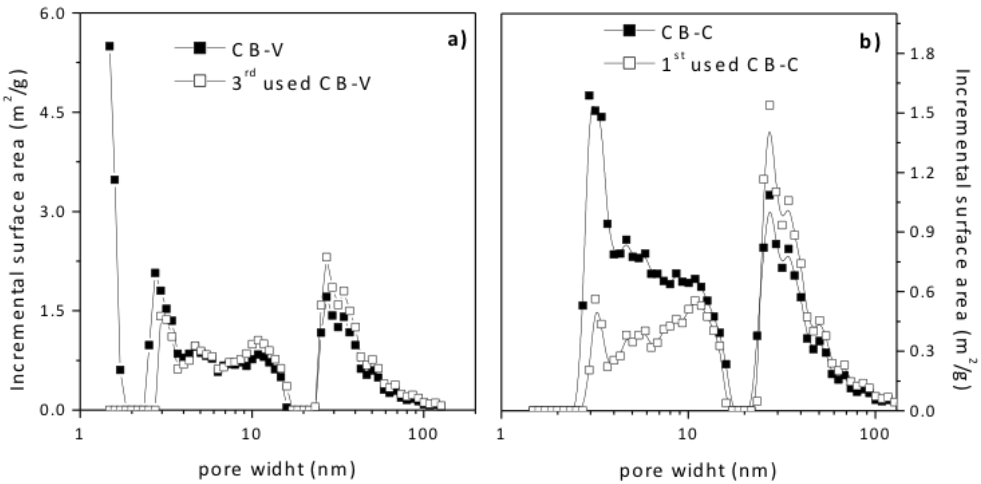


Figure S3. DFT pore size distribution of CB-V (a) and CB-C (b)

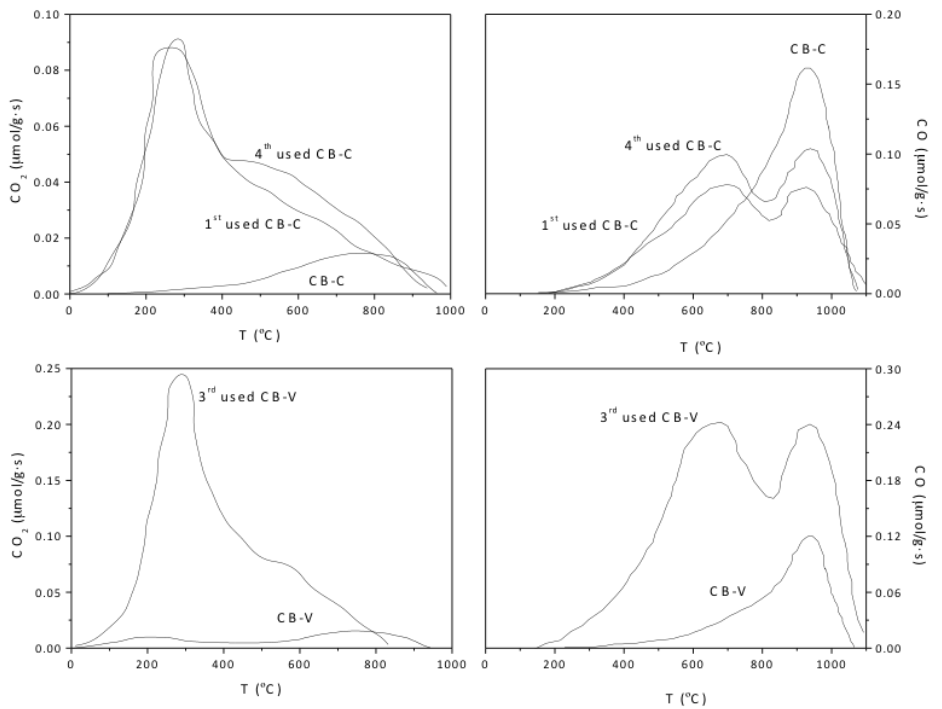


Figure S4. TPD profiles of CB-C (a) and CB-V (b)

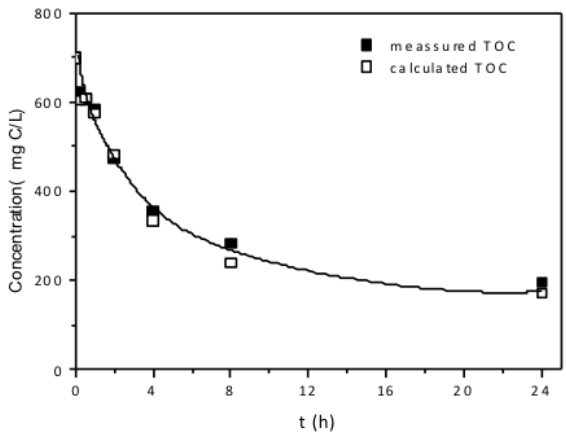
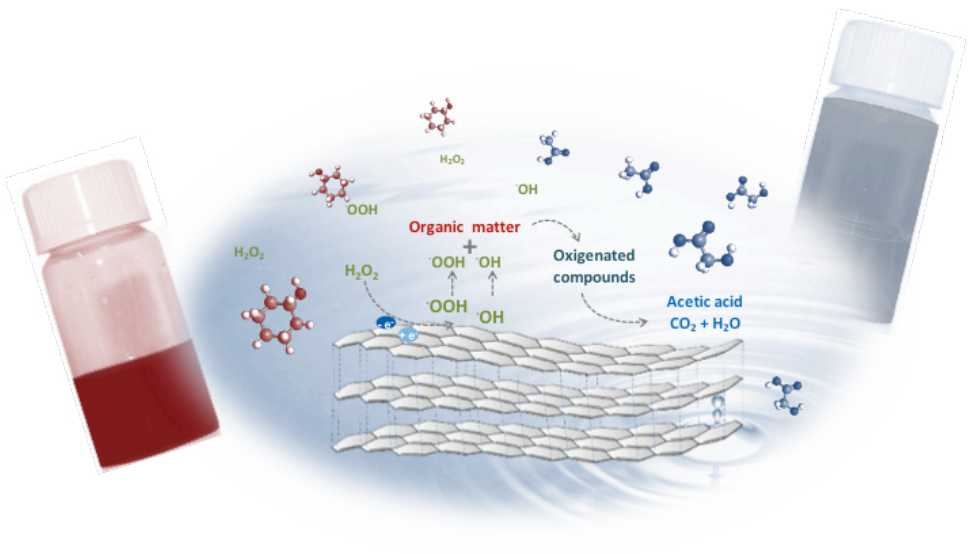


Figure S5. Time-evolution of measured and calculated TOC values upon CWPO of phenol with CB-C at the operating conditions of Figure 9.

Bloque III

Tratamiento de aguas residuales de la industria vitivinícola mediante oxidación húmeda con peróxido de hidrógeno con catalizadores basados en materiales carbonosos

Capítulo VI. Treatment of high-strength winery wastewater by wet oxidation at mild temperature



Treatment of real winery wastewater by wet oxidation at mild temperature.

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ARTICLE INFO

Keywords
Winery wastewater
catalytic wet air oxidation
catalytic wet peroxide oxidation
carbon catalysts
ecotoxicity.

ABSTRACT

This study explores the treatment of high-strength real winery wastewater (COD0≈35 g/L, TOC0≈11 g/L) by wet oxidation processes. Wet air oxidation (WAO), catalytic wet air oxidation (CWAO), H2O2-promoted CWAO, wet peroxide oxidation (WPO) and catalytic wet peroxide oxidation (CWPO) were the options tested using different carbon-based catalysts, viz. activated carbon, carbon black and graphite. Their suitability was analysed in terms of polyphenol, chemical oxygen demand (COD) and total organic carbon (TOC) abatement upon 4 h reaction time. The results showed that hydrogen peroxide was the unique oxidant capable of achieving an effective reduction of the organic load. The graphite tested was the most active catalyst, most probably due in great part to its Fe content (0.4 wt%), resistant to leaching. CWPO with that graphite was tested at different conditions following the evolution of COD, TOC and ecotoxicity. The best results were obtained by using graphite at 5 g/L, the original pH of the wastewater (3.8), 125 ºC and the stoichiometric amount of hydrogen peroxide distributed in stepwise additions. Under those conditions, 80% COD and TOC removals with 85% of hydrogen peroxide efficiency were achieved after 4 h reaction time, giving rise to colourless effluents of very low Microtox ecotoxicity.

1. Introduction

The wine industry generates large volumes of wastewaters, between 1.3 and 1.5 L/L of wine [1]. These effluents are originated most in particular from the washing of the presses used for crushing the grapes and, in lesser extent, from the rinsing of fermentation tanks, barrels and other equipment components [2, 3]. Winery wastewater is characterized by a widely variable high organic strength (800 to 25,000 mg/L COD), high salinity (3,000-4,000 μS/cm) and sodicity (SAR=8-9). The typical components are suspended solids, polyphenols, organic acids, alcohols, sugars (maltose, glucose, fructose), aldehydes, soaps and detergents, nitrogen compounds and inorganics, including some traces of heavy metals [4, 5].

The wine industry recognizes the priority of the environmental and economical sustainable management of its wastewater [6] and, therefore, medium and large-scale wineries are usually equipped with biological treatment systems (aerobic, anaerobic or combinations of both). However, the seasonal variation of winemaking provokes important fluctuations in the quantity and quality of the effluents. This, in addition to the presence of recalcitrant compounds, especially polyphenols, make it difficult to find effective solutions capable of achieving a high reduction of the organic load [5, 7]. Advanced oxidation processes (AOPs) are currently being proposed as alternative to biological treatment for these wastewaters [4, 5].

Ozonation [2, 8-10], photocatalysis [3, 10, 11] and combined processes, i.e. O3/TiO2/UV [10], O3/UV/H2O2 [2], UV/TiO2/H2O2 [12] have been typically tested with synthetic wastewaters prepared from commercial wine or grape juice, and only few studies have been conducted with real winery wastewater [2, 9, 12]. The combined processes have demonstrated to be more efficient. COD and TOC reductions close to 60% have been reported as the best results with real winery wastewater of moderate initial COD (≈4,000 mg/L) [2, 12].

The Fenton process is commonly characterized by its simplicity and low cost compared to other AOPs [13, 14]. However, fairly poor results have been obtained so far with winery wastewaters because of the refractoriness of a great part of the organic matter of those effluents under the common operating conditions of the conventional Fenton process. Combination with UV light radiation has been checked to improve the efficiency of that process [7, 11, 15-18]. Alternatively, Fenton oxidation has been proposed as post-treatment for the purpose of removing the complex organic molecules remaining after biological oxidation [19-21]. Wastewaters with a low initial COD (600 to 1,500 mg/L) have been treated by this way leading to COD reductions within a fairly wide range (60 to 90%) depending on the dose of hydrogen peroxide, the [H2O2]/Fe ratio and the initial COD.

The current work investigates the treatment of high-strength real winery wastewater by wet oxidation processes for the purpose of identifying an effective solution capable of dealing with the seasonal fluctuations of the winemaking effluents allowing a high reduction of their organic load with almost complete depletion of polyphenols. Non-catalytic and catalytic wet air oxidation (WAO and CWAO, respectively) and wet peroxide oxidation (WPO and CWPO) have been tested. In WAO, high temperatures and pressures (T=120-300 ºC, P=0.8-20 MPa) are required [22] while WPO works under rel-

atively milder operating conditions (T=50-125 ºC, P=0.1-0.5 MPa) using hydrogen peroxide [23]. Different carbon-based materials, viz. activated carbon, carbon black and graphite have been tested as catalysts. Those materials have demonstrated to be active in CWAO [24] and CWPO [25, 26] of phenol. Hydrogen peroxide-promoted CWAO with the different carbon materials tested has also been studied. The beneficial effects of hydrogen peroxide as free-radicals promoter combined with oxygen in the presence of activated carbons have been proved in previous works for the treatment of phenolic wastewaters [27, 28]. Once selected the most efficient process in terms of COD and TOC removals, the operating conditions (temperature, pH, initial COD, hydrogen peroxide dose and the way of feeding the reagent) will be investigated for the sake of learning on their influence on the efficiency of the process by following the evolution of COD, TOC and ecotoxicity.

2. Experimental

2.1 Winery Wastewater

The winery wastewater was sampled from a wine factory located in Badajoz (Spain). It is a brownish acid effluent of unpleasant odor. A representative analysis is given by: pH=3.8, ecotoxicity=52 TU, conductivity=7.38 mS/cm, inorganic constituents=4.5 g/L (N=0.32 g/L, K=2.5 g/L and P=0.28 g/L), COD=35 ± 2.2 g/L and TOC=11.3 ± 0.9 g/L. Close to 45% of the total organic carbon was identified as glycolic acid (5 g/L), acetic acid (3.5 g/L), malonic acid (1.2 g/L) and polyphenols (0.7 g/L equivalent phenol). Another acids (propanoic, 2-hydroxypropanoic, ethyl ester 2-hydroxypropanoic, butanoic, succinic, pentanoic, hexanoic, methyl phenylglyoxylate) and alcohols (ethanol, benzyl alcohol, phenylethyl alcohol, 2-ethyl-phenol, 2-butanol, glycerol) were detected in trace amounts.

2.2. Catalysts characterization

Three commercial carbon materials were tested as catalysts: activated carbon (AC, Panreac, ref.: 121237), carbon black (CB, Chemviron, ref.: 0.45527) and graphite (G, Sigma-Aldrich, ref.: 282863). Before use, the samples were sieved and the particle size ranging from 80 to 100 mm was selected for the experiments.

The specific surface area (SBET) values were obtained from the 77 K N2 adsorption/desorption isotherms using a Micromeritics Tristar apparatus. The micropore volume and the external or non-microporous surface area were obtained by the t-method. Elemental analyses of the as-received materials were performed in a LECO Model CHNS-932 apparatus. Elements identification and iron content in the carbon ashes were performed by TXRF (Extra-II Rich & Seifert spectrometer).

2.3. Oxidation experiments

The oxidation experiments were carried out in a 75 mL autoclave reactor (Berghof). The reactor consists of a stainless-steel pressure vessel (PTFE) placed on a magnetic stirrer and surrounded by an electric resistance heating block provided of the corresponding control system. Pressure was measured by a transducer. Six ports Valco valve VICI with two positions allows the gas flow pass through the reactor or bypass it. The inlet gas flow-rate (92 NmL/min of pure N2 or O2) bubbling into the liquid was adjusted by mass flow controllers (Hi-Tec Bronkhorst). In a typical CWAO experiment, 75 mL of wastewater at the testing pH and the catalyst were charged to the vessel. Then, the reactor was stoppered, heated and pressurized under nitrogen atmosphere to the desired conditions. After stabilization, the N2 flow was switched into O2 and the stirring was started at 1500 rpm. This was considered the starting reaction time. In the H2O2-promoted CWAO and CWPO experiments, the experimental procedure was similar to the above described but 60 mL of wastewater were charged to the reactor and, once established the selected operating conditions, 15 mL of hydrogen peroxide aqueous solution of the appropriate concentration were fed with a chromatographic pump (GILSON, model 307). The non-catalytic experiments were performed as in the corresponding catalytic process but obviously in the absence of catalyst.

Liquid samples were periodically withdrawn from the reactor and immediately injected in a vial (submerged in crushed ice) containing a known volume of cold distilled water. The diluted samples were filtered (0.45 mm Nylon filter) and subsequently analyzed by different techniques.

The operating conditions for the WAO, CWAO and H2O2-promoted CWAO experiments were pH=3.8, 160 ºC and 1 MPa with a pure oxygen flow of 92 NmL/min. In the case of H2O2 promoted-CWAO, H2O2 was added at 20% of the stoichiometric amount relative to the initial COD. The WPO and CWPO runs were performed at pH=3.8, 80 ºC, 0.1 MPa and 58 g/L H2O2 (100% of the stoichiometric amount of H2O2 relative to the initial COD). The catalyst, when used, was added in all cases at 5 g/L. Latter, the operational window tested for the CWPO with graphite was: pH0=2.2-7, T=80-125 ºC, P=0.1-0.7 MPa, [COD]0=3.5-35 g/L and [H2O2]0=0-1.6 times the stoichiometric amount. Two ways of feeding hydrogen peroxide were tested: once-through at the start of the experiment and stepwise upon the reaction time (4 h).

2.4. Chemical analyses

Total organic carbon (TOC) was measured using a TOC analyzer (Shimadzu, model TOC VSCH). The hydrogen peroxide concentration was determined by colorimetric titration using the TiOSO4 method [29]. Chemical oxygen demand (COD) measurements were accomplished according to the standard method (ISO 6060). The COD values were corrected discounting the contribution of the remaining hydrogen peroxide (CODcorrected=CODmeassured-0.4635·CH2O2). Identification and quantification of inorganic constituents such as

metals in the initial wastewater and in the reactor effluents was performed by TXRF. Polyphenolic compounds were measured by the Folin-Reagent test at 700 nm using a UV-VIS spectrophotometer (Shimadzu, mod. UV-1603). Short-chain organic acids were determined by Ionic Chromatography (IC) with anionic chemical suppression using a conductivity detector (Metrohm, mod. 883 BASIC IC Plus). A Metrosep A supp 5-250 column (25 cm long, 4 mm diameter) was used as stationary phase and 0.7 mL/min of an aqueous solution 3.2 mM of Na2CO3 and 1 mM of NaHCO3 as mobile phase.

The identification of species was performed by gas chromatography/ion trap mass spectrometry (GC/MS using a CP-3800/Saturn 2200, Varian apparatus equipped with an automatic injector CP-8200/SPME, solid-phase microextraction). The capillary column used was a Factor Four VF-5 ms, Varian (30 m length and 0.25 mm i.d.). The carrier gas (helium) flow rate in the GC was 1 mL/min. The solid-phase microextraction (SPME) was carried out with a fiber cartridge (poly(dimethylsiloxane) red), using adsorption and desorption times of 30 and 5 min, respectively. The sample injection was conducted at 220 ºC. The temperature program used in the GC-MS analyses ramped as follows: 40 ºC for 5 min, increased to 250 ºC at 15 ºC/min, held at 250 ºC for 10 min, increased to 300 ºC at 20 ºC/min, and held at 300 ºC for 2 min. Additional measurements were performed extracting the aqueous samples with solid-phase cartridges (C18, Waters), eluted with different organic solvents (n-hexane and methanol). The identifications were assessed with the aid of the database library NIST.

2.5. Ecotoxicity

The ecotoxicity of the effluents was determined in a Microtox M500 Analyzer (Azur Environmental) following the standard Microtox test (ISO 11348-3, 1998). This bioassay is based on the decrease of light emission by Photobacterium phosphoreum as the result of exposure to a toxicant at 15 ºC for 15 min. The toxicity units of the sample are calculated from: TU=100/IC50, where IC50 is defined as the sample dilution percentage that yields 50% reduction of the light emitted by the microorganisms. Before measuring the toxicity, the residual hydrogen peroxide was removed with sodium bisulfite and the pH value of all the samples was adjusted between 6 and 8 according to the test specifications. The microorganisms were purchased from Microtox Acute Reagent supplied by I.O. Analytical. More detailed information about this assay and its application to wastewater can be found elsewhere [30].

3. Results and discussion

3.1. Catalyst characterization

The characterization of the carbon materials used as catalysts is summarized in Table 1. These materials show fairly different porous structure. The activated carbon has a well-developed microporosity but also an important contribution of mesoporosity, as indicates the high value of external or non-micropore surface area (Aext) which represents more than one-half the BET surface area (SBET). As expected, carbon black and graphite are non-microporous solids with low surface area, specially the second one.

The elemental analyses confirm that the three materials consist essentially of carbon. Some significant differences can be observed in the ash content, where it is important the presence of Fe in the graphite at 0.4% of the total dry weight. Special attention must be paid to this metal due to its catalytic activity for hydrogen peroxide decomposition into hydroxyl radicals.

Table 1
Characterization of the carbon materials used as catalysts (analyses in % weight, dry basis)

Sample	S_{BET} (m^2/g)	A_{ext} (m^2/g)	$V_{micropore}$ (m^2/g)	C (%)	Ashes (%)	Fe (%)
Activated Carbon (AC)	931	472	0.161	93.7	1.0	< 0.01
Carbon Black (CB)	75	75	-	≈99	0	0
Graphite (G)	12	12	-	97.2	0.50	0.40

3.2. Oxidation treatments

In a first attempt to reduce the organic load of the wastewater and then, the amount of oxidant (hydrogen peroxide or oxygen) required for the chemical oxidation, several pretreatments like adsorption with activated carbon and precipitation with Ca(OH)2 were checked. Fairly low COD and TOC reductions (less than 20%) and no significant ecotoxicity variation were observed, so that the raw wastewater was directly submitted to the different oxidation treatments investigated.

Figure 1 depicts the results obtained upon each of the oxidation processes tested after 4 h reaction time under the operating conditions indicated in the Experimental Section. Control experiments were also carried out to analyze the stability of the wastewater at the operating temperature. The thermal decomposition was negligible at 80 ºC but increased up to 20% of the initial COD at 160 ºC.

The results show frankly low reductions of COD and TOC upon WAO at 160 ºC and 1 MPa (XCOD≈30%), moreover taking into account that a great part of this COD reduction can be attributed to the aforementioned thermal decomposition. The presence of a carbon catalyst did not particularly improve the performance of the process. Only polyphenols disappearance increased somewhat in the presence of activated carbon or carbon black, this being due mostly to adsorption [25]. A high reduction of polyphenols may be eventually important for a subsequent biological treatment since those compounds are resistant to biodegradation [5, 7].

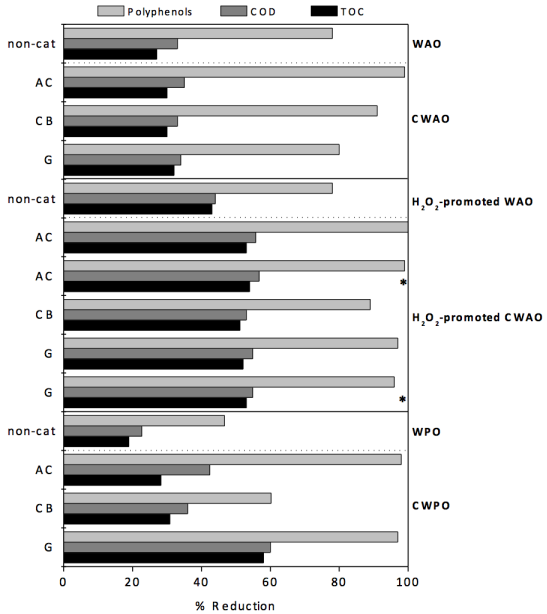

Figure 1. Results obtained upon treatment of the winery wastewater by the oxidation processes tested after 4 h reaction time. [(*) the presence of nitrogen instead of oxygen]

The addition of hydrogen peroxide at only 20% of the stoichiometric amount improved significantly the COD and TOC removals (c.f. WAO and H2O2-promoted WAO in Figure 1) allowing up to about 40% reduction of both. With the carbon materials tested the results were appreciably better, reaching 55-60% COD and TOC removals. These results are comparable to the reported from photo-assisted oxidation treatments like O3/UV/H2O2, O3/UV/TiO2 and H2O2/UV/TiO2 [2, 10, 15]. H2O2-promoted WAO and CWAO experiments performed under N2 instead of O2 flow showed no significant differences in terms of oxidation and mineralization, indicating that the improved degradation of the organic matter was essentially due to hydrogen peroxide without significant synergistic effects of this reagent and oxygen. Those synergistic effects had been demonstrated in previous works on H2O2-promoted CWAO of phenol [27, 28] but do not seem to apply with this high strength winery wastewater.

Regarding polyphenols, almost complete conversion was observed in the H2O2-promoted CWAO experiments with activated carbon and graphite. In the former, adsorption plays an important role while in the second the Fe content of the graphite tested (see Table 1) must have a determining effect.

CWPO with graphite leads to somewhat higher COD and TOC reductions and at substantially lower temperature than H2O2-promoted CWAO (80 vs. 160 ºC). As indicated before, the wastewaters tested is highly stable at 80 ºC, therefore, the degradation of organic matter upon CWPO is essentially due to the oxidation process without significant contribution of thermal decomposition, which occurs in CWAO at 160 ºC.

The improved efficiency and the considerable reduction of temperature compensate the need of hydrogen peroxide in CWPO, which in the experiments of Figure 1 was added only at 20% of the stoichiometric amount relative to the initial COD. The higher activity of the graphite compared to the activated carbon and carbon black tested is consistent with the results obtained in a previous work [31] where the catalytic activity of these three materials for hydrogen peroxide decomposition was analysed by cyclic voltammetry. In that study, it was demonstrated that the iron content of the graphite tested, was the most important feature explaining its higher activity in spite of its much lower surface area.

TXRF analyses of the fresh and used graphite, as well as of the corresponding CWPO effluents indicated that iron was not leached during the process. In fact, the activity of graphite was maintained upon three successive cycles where COD and TOC reductions remained invariable at around 60% after 4 h reaction time (Figure S1 of the Supplementary Data).

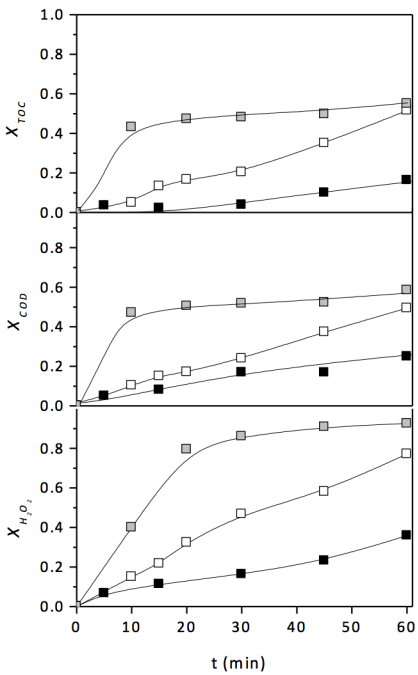

Figure 2. Effect of temperature on TOC and COD reduction and hydrogen peroxide decomposition upon CWPO with graphite. Operating conditions: P=0.7 MPa, pH0=3.8, CCAT=5 g/L and H2O2:COD=stoichiometric. (□) 80 ºC (▫) 100 ºC (□) 125 ºC.

3.3. CWPO with graphite

The preceding results support the potential application of CWPO for the treatment of winery wastewater using the Fe-containing graphite as catalyst. To learn more on that potential application, the effect of temperature, pH, initial COD, hydrogen peroxide dose and the way of feeding this reagent, were investigated following the TOC and COD reductions as well as the ecotoxicity of the effluents. This last parameter provides valuable information regarding further application of a subsequent biological treatment.

3.3.1. Effect of temperature

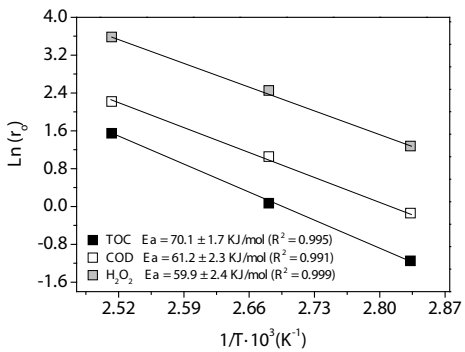

Figure 3. Arrhenius plot from the CWPO experiments of Figure 2.

Three different temperatures (80, 100 and 125 ºC) were tested using the stoichiometric dose of hydrogen peroxide. The conversion profiles upon 1 h reaction time are given in Figure 2. The results show that increasing the temperature within the range tested improves significantly the oxidation rate in the early stages of the process, consistently with the faster decomposition of hydrogen peroxide. The final COD and TOC reductions after almost complete consumption of H2O2 (1 h reaction time at 100 and 125 ºC and at 4 h at 80 ºC) were similar (around 60%) since that is governed by the H2O2 dose. No Fe leaching was detected within the temperature range tested and no more than 5% of the COD and TOC removals can be attributed to thermal decomposition at the highest temperature tested (125 ºC) after 4 h.

Figure 3 shows the Arrhenius plots of the initial rates of hydrogen peroxide decomposition and TOC and COD reductions. The corresponding values of the apparent activation energy are included.

The temperature also affects to the distribution of by-products. It was seen that increasing the temperature from 80 to 125 ºC reduced dramatically the percentage of the unidentified TOC after complete hydrogen peroxide consumption (42% at 80 ºC vs. only around 5% at 100 and 125 ºC). The identified TOC corresponds mainly to acetic acid (85% of the residual TOC), which is an expected by-product from the oxidation of ethanol [11] and from the breakdown of larger organic acids such as tartaric, malic and lactic [17] contained in the wastewater and some of them also formed upon oxidative degradation of more complex species.

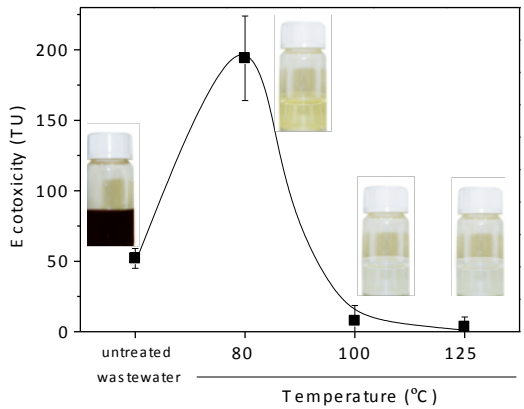

Figure 4. Ecotoxicity of the effluents from CWPO with graphite after 4 h at different temperatures (P=0.7 MPa, pH0=3.8, CCAT=5 g/L, H2O2:COD=stoichiometric).

Figure 4 shows the ecotoxicity of the resulting effluents after 4 h reaction time at different temperatures. Pictures of the corresponding samples are included where it can be seen that CWPO leads to almost colorless effluents from the dark brown initial wastewater. As observed, increasing the temperature has a marked beneficial effect on the reduction of ecotoxicity within the range 80-100 ºC. Interestingly, the application of CWPO at 80 ºC is accompanied by a remarkable increase of ecotoxicity in spite of the significant reductions of COD, TOC and color. This fact indicates the formation of some reaction by-products of higher toxicity than the initial components of the wastewater. In addition, the ecotoxicity of the effluent from non-catalytic WPO at 80 ºC was also determined, yielding a significantly higher value (925 TU). An attempt to identify the nature of the ecotoxic species, several effluent samples were analyzed by GC-MS. Most of the relevant peaks observed in the chromatograms of the raw wastewater (identified as phenylethyl alcohol, 4,4 dimethylbenzyl, methyl phenylglyoxylate, benzyl alcohol, 2-ethyl-phenol) did not appear in the effluents, while others corresponding to short chain organic acids, such as acetic and propanoic acid were increased (see Figure S2 in the Supplementary Data). It should be noted the presence of an unidentified peak in the ecotoxic effluents which was not observed in the raw wastewater and in the effluent from CWPO at 125 ºC. The signal of that peak (m/z=44) increased according to the ecotoxicity of the effluent (see Figure S3 in the Suppplementary Data).

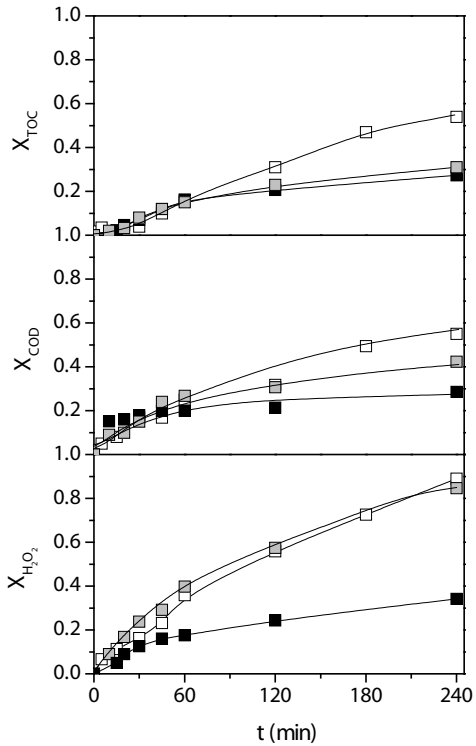

Figure 5. Effect of initial pH on TOC and COD reduction and hydrogen peroxide decomposition upon CWPO with graphite. Operating conditions: T=80 ºC, P=0.1 MPa, CCAT=5 g/L and H2O2:COD=stoichiometric. (■) pH0=2.2 (□) pH0=3.8 (■) pH0=7.

3.3.2. Initial pH

It is well known that wet peroxide oxidation is sensitive to the pH and usually acid conditions are required [32]. The effect of this variable was explored within the range of 2.2 to 7. The starting pH value was adjusted (but not buffered) with 1M solution of HCl or NaOH. The results obtained at different initial pH values and 80 ºC are depicted in Figure 5. As can be seen, at the lowest pH tested (2.2), the decomposition of hydrogen peroxide becomes much slower but this circumstance does not affect so dramatically to TOC and COD reductions. The best results were obtained at pH 3.8, which is that of the wastewater as received. This simplifies the potential application of CWPO to this type of waste. At neutral pH, the rate of hydrogen peroxide decomposition was similar as at 3.8, but fairly lower efficiency of TOC and COD reductions was observed due to the favored decomposition of hydrogen peroxide into oxygen and water.

3.3.3. Effect of the initial organic load

Winery wastewaters are characterized by fluctuations in flow-rate and organic loads which represent an inconvenience regarding the application of currently established technologies like anaerobic digestion. Thus, it is important to know how the organic load affects to the efficiency of the CWPO. With this purpose, wastewater with different initial COD values of 35, 17 and 3.5 g/L, prepared by dilution of the as received wastewater with distilled water have been charged to the reactor. Figure 6 shows that changes in the initial COD do not affect to the percentage reduction of TOC and COD achieved using the corresponding stoichiometric dose of hydrogen peroxide. This confirms the refractory character of a fraction of the organic matter of these wastewaters in terms of TOC. From the operational point of view, the same installation would be adequate for the treatment of any winery wastewater generated during the working season by adjusting the appropriate dose of hydrogen peroxide to the inlet organic load (COD, TOC).

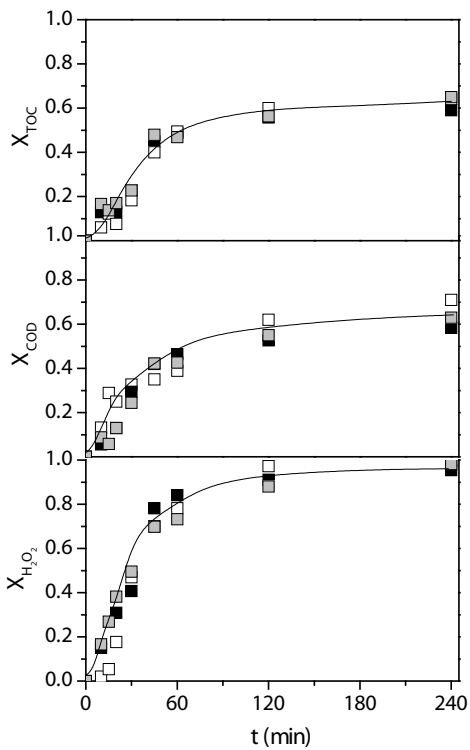

Figure 6. TOC and COD evolution and hydrogen peroxide decomposition in CWPO at different initial organic loads (T=100 ºC, pH0=3.8, P=0.7 MPa, CCAT=5 g/L and H2O2:COD=stoichiometric). (■) COD0=35 g/L (■) COD0=17.5 g/L (□) COD0=3.5 g/L.

3.3.4. Hydrogen peroxide dose

Figure 7 shows the results obtained at 125 ºC with different hydrogen peroxide doses within a wide range up to 1.6 times the stoichiometric. As can be seen, the TOC and COD reductions increased linearly with the amount of hydrogen peroxide up to the stoichiometric amount and beyond that a further small variation was observed. The asymptotic value at around 70% conversion is consistent with the existence of a refractory organic fraction corresponding to oxidation by-products and to initially present species, mainly short-chain organic acids, like acetic acid. The efficiency of hydrogen peroxide consumption (h), defined as the amount of COD removed per hydrogen peroxide consumed, progressively decreases from 0.9 to 0.45 values with the oxidant dose (Figure 7).

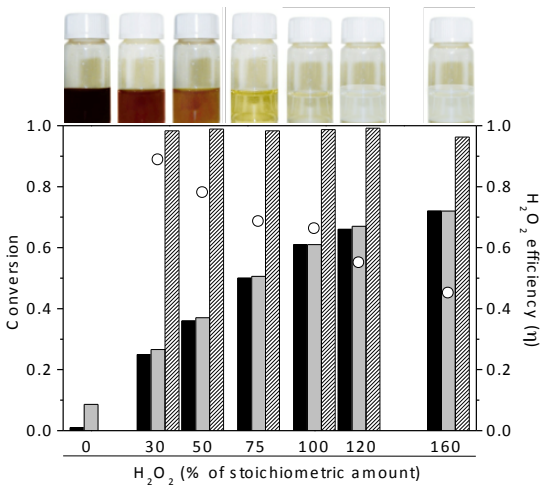

Figure 7. Results of CWPO (4 h) at 125 ºC with different hydrogen peroxide doses (pH0=3.8, P=0.7MPa and CCAT=5 g/L). (■) TOC (▩) COD (□) H2O2 (○) H2O2 efficiency.

The effect of the hydrogen peroxide dose was also observed on the residual color of the effluent, which decreased progressively from brown to colorless when using at least the stoichiometric amount of hydrogen peroxide (Figure 7).

The dose of hydrogen peroxide showed a remarkable effect on the ecotoxicity of the resulting effluents as can be seen in Figure 8. At frankly substoichiometric doses highly toxic oxidation intermediates are formed which need further addition of hydrogen peroxide to be destroyed. These intermediates most probably include aromatic condensation by-products, responsible of the brownish color of the effluent (Figure 7), which finally breakdown as the hydrogen peroxide is increased.

The optimum dose of hydrogen peroxide can be established around the stoichiometric amount. This allows achieving more than 60% mineralization and complete color removal. Above the stoichiometric hydrogen peroxide dose, very low improvement is gained in terms of COD and TOC reductions due to the refractory character of the remaining organic matter.

The way of addition of hydrogen peroxide is also an important variable because it affects to the efficiency of hydrogen peroxide consumption. Figure 9 shows the TOC and COD conversions as well as hydrogen peroxide consumption and the efficiency values when the stoichiometric amount of hydrogen peroxide was stepwise added upon 4 h reaction time instead of in a simple addition at the start of the experiment as in the runs so far. As can be observed, this strategy is highly convenient since it allows achieving higher TOC and COD conversions with the same amount of H2O2. The stepwise feeding allows maintaining a high (0.85-1) efficiency of hydrogen peroxide consumption versus the 60% achieved under once-through addition of the reagent at the start of the experiment.

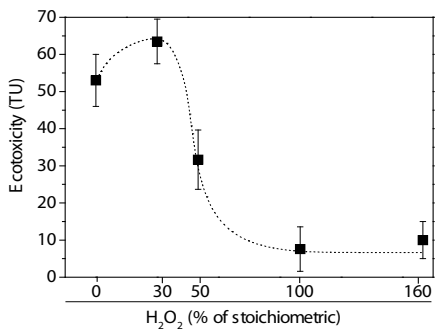

Figure 8. Ecotoxicity of the CWPO (4 h) effluents at different hydrogen peroxide doses. Operating conditions: T=125 ºC, pH0=3.8, P=0.7 MPa and CCAT=5 g/L.

4. Conclusions

Different oxidation processes (WAO, CWAO, H2O2 promoted WAO, H2O2 promoted CWAO, WPO and CWPO) have been tested for the treatment of high-strength real winery wastewater, being CWPO with Fe-bearing graphite the one yielding the best results. Fe leaching from the graphite catalysts was negligible.

Increasing temperature within the 80-125 ºC range improves significantly the results obtained in terms of COD, TOC and ecotoxicity reductions. A similar effect was observed by increasing the hydrogen peroxide dose up to the stoichiometric amount relative to the initial COD. Further improvements beyond that those were very small. Complete degradation of polyphenols, 80% COD and TOC removals, total colour and odour elimination and very low ecotoxicity values were achieved with 85% hydrogen peroxide efficiency in 4 h reaction time at 125 ºC, 0.7 MPa, 5 g/L of graphite, at the pH

of the wastewater as received (3.8) and by stepwise distributed addition of the stoichiometric amount of hydrogen peroxide relative to the initial COD.

CWPO appears a promising option for the treatment of this type of wastewaters subjected to wide fluctuation of daily volumes and organic load. No significant changes on the percentage of COD and TOC reductions were observed within a broad range of initial COD (3.5-35 g/L) under the corresponding stoichiometric dose of hydrogen peroxide.

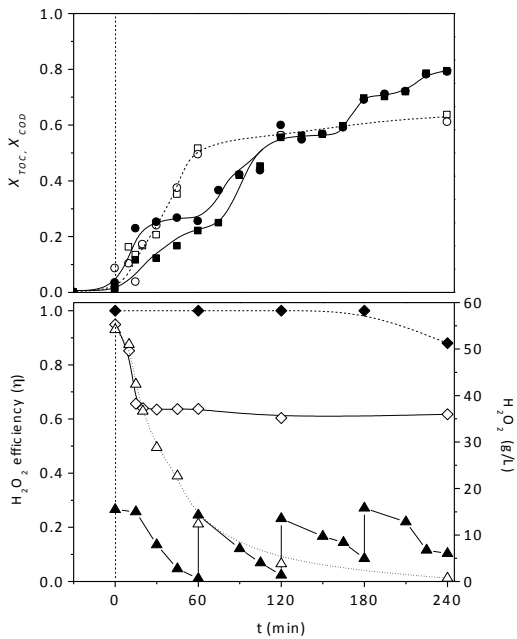

Figure 9. Results of CWPO with graphite under stepwise (solid symbols) and once-through (open symbols) feeding of the stoichiometric amount of H2O2 (COD: circles, TOC: squares; H2O2 concentration: triangles and hydrogen peroxide efficiency: rhombus. Operating conditions: T=125 ºC, pH0=3.8, P=0.7 MPa and CCAT=5 g/L.

Acknowledgements

The authors wish to thank the Spanish MICINN for the financial support through the projects CTQ2008-03988/PPQ and CTQ2010-14807. The Comunidad Autónoma de Madrid is also gratefully acknowledged for the financial support through the project S2009/AMB-1588.

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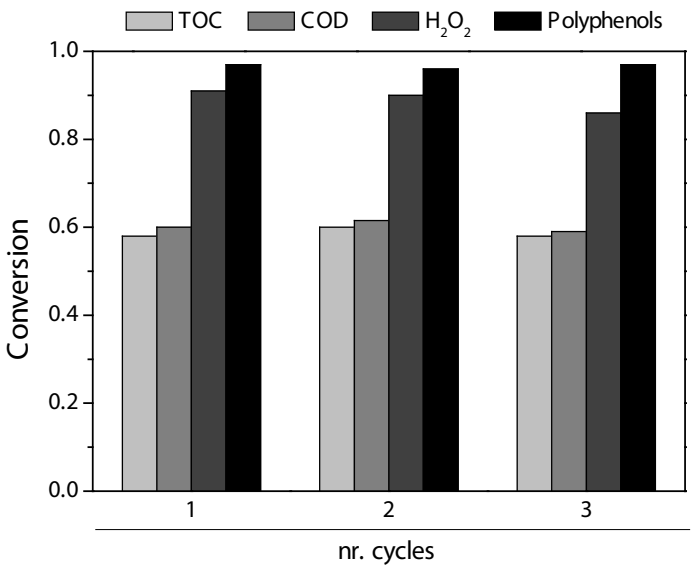


Figure S1. Stability study of graphite. Operating conditions: T= 80 ºC, P=0.7 MPa, pH=3.8, C_{CAT}=5 g/L and H_2O_2:COD=stoichiometric.
Note: after each run, the catalyst was separated by filtration and dried at 60 ºC for 24 h without any further treatment.

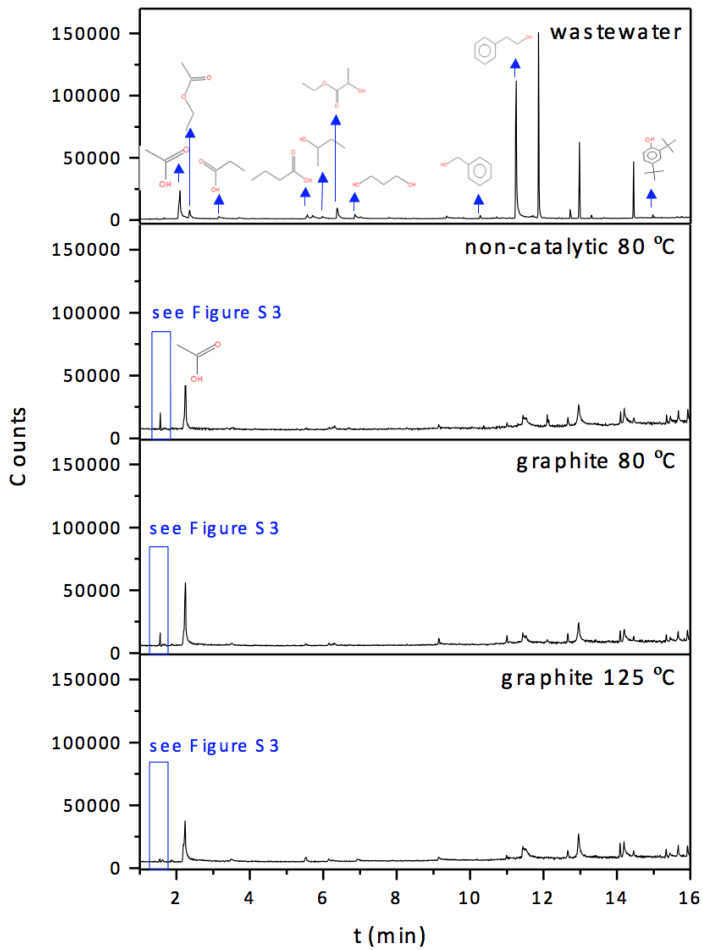


Figure S2. GC chromatograms (SPME) of raw wastewater, WPO and CWPO effluents.

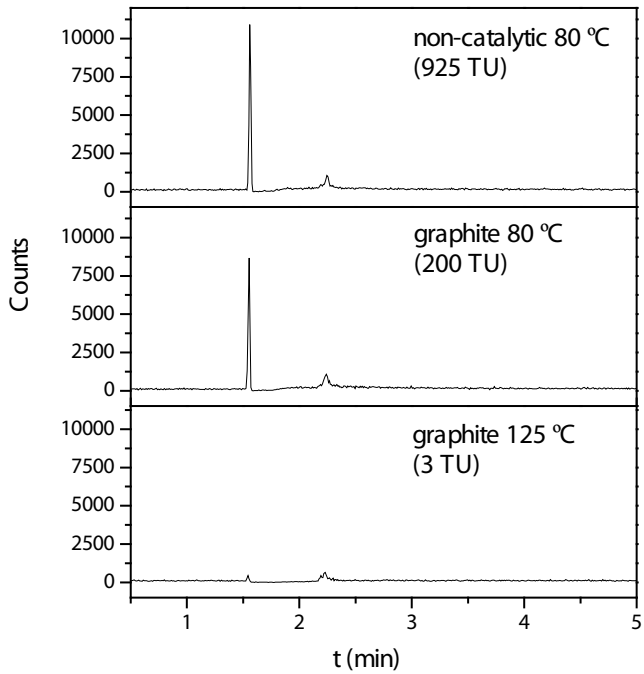


Figure S3. GC chromatograms (SPME) of WPO and CWPO effluents showing the peak assigned to the highly ecotoxic unidentified species (m/z=44).

5

Resumen/ Summary

El empleo de catalizadores heterogéneos para el tratamiento de aguas residuales industriales contaminadas por compuestos orgánicos persistentes mediante el proceso de oxidación húmeda con peróxido de hidrógeno (proceso CWPO) permite superar las principales desventajas asociadas al empleo de catalizadores homogéneos en el proceso Fenton (sales de Fe^{2+}), como son la pérdida continua de catalizador y la necesidad de separar el mismo del efluente de reacción, la generación y gestión de lodos de hidróxido de hierro generados en la etapa de neutralización, y el hecho de tener que operar en un estrecho intervalo de pH (3-4). Sin embargo, la utilización de catalizadores heterogéneos se encuentra supeditada a que éstos presenten una elevada actividad, adecuada estabilidad y aseguren un eficiente consumo de peróxido de hidrógeno. A pesar de los grandes esfuerzos de investigación realizados en este campo, el desarrollo de catalizadores económicos que cumplan estas características, sigue siendo un reto.

En esta Memoria se da cuenta del trabajo realizado sobre el estudio de catalizadores basados en materiales carbonosos para su empleo en procesos de oxidación húmeda con peróxido de hidrógeno. Con el fin de obtener un catalizador activo, estable y eficiente se ha procedido al empleo de materiales carbonosos como soporte de fases activas metálicas resistentes a la lixiviación (catalizadores de oro soportados sobre carbón activado) y como catalizadores en estos procesos. En este último caso, se ha estudiado no sólo el carbón activado sino también otro tipo de sólidos carbonosos, como negros de humos y grafitos. Los catalizadores mencionados han sido empleados en el tratamiento de aguas residuales contaminadas por compuestos modelo, como fenol y alcohol bencílico, y de aguas residuales reales procedentes de la industria vitivinícola.

Estudios previos sobre el empleo de catalizadores basados en nanopartículas de oro en el proceso CWPO han mostrado que cuando éstas se encuentran inmovilizadas sobre determinados soportes, ***i.e.*** diamante nanoparticulado o hidroxiapatita, pueden considerarse interesantes candidatos para la oxidación húmeda con peróxido de hidrógeno. Esto es debido, por un lado, a las propiedades redox del oro cuando se presenta en tamaño nanoparticulado, que permiten catalizar la reacción de descomposición de peróxido de hidrógeno a radicales hidroxilo e hidroperóxido y, por otro, a su resistencia a la lixiviación, principal causa de desactivación de los catalizadores heterogéneos en el proceso CWPO.

En este trabajo se ha estudiado la posibilidad de inmovilizar nanopartículas de oro sobre un soporte más económico y disponible que los anteriormente empleados, el carbón activado. En primer lugar se ha estudiado el origen de la actividad catalítica de las nanopartículas de oro inmovilizadas sobre diferentes soportes, con el fin de

explicar la disparidad de resultados mostrados en los pocos trabajos publicados sobre el empleo de este metal en procesos de oxidación húmeda con peróxido de hidrógeno y, poder desarrollar así, catalizadores heterogéneos basados en nanopartículas de oro con alta actividad y eficiencia, inmovilizadas sobre soportes asequibles. Posteriormente, se llevó a cabo un estudio de las condiciones de operación bajo las que se debe trabajar con el catalizador Au/carbón activado (Au/CA), con el fin de asegurar una alta eficiencia en el consumo de peróxido de hidrógeno. Por último se estudió su estabilidad y se propuso un esquema de reacción para la oxidación húmeda de fenol con peróxido de hidrógeno, a partir de la cual se discriminó un modelo cinético.

Para llevar a cabo el estudio sobre el origen de la actividad catalítica de las nanopartículas de oro soportadas se emplearon catalizadores comerciales Au/TiO_2 (Mintek, 0,8% Au, d_{Au}=3,1±1,8), Au/Fe_2O_3 (World Gold Council, 4,48% Au, d_{Au}=3,6±0,9) y catalizadores Au/CA sintetizados en el laboratorio mediante el método de impregnación-secado. Dicho método consistió en poner en contacto la disolución coloidal de nanopartículas de oro de diferente tamaño con la cantidad requerida de carbón activado (Merck, ref.: 102514) con el fin de obtener un catalizador con un contenido final en oro de 0,5% en peso. Se emplearon disoluciones acuosas coloidales con nanopartículas de oro de diferentes tamaños: 3 nm, con citrato de sodio como agente protector (suministrado Strem Chemicals Inc.) y 5, 7 y 10 nm, protegidas por ácido tánico, (suministrado por Nanocomposix). El contacto entre la suspensión coloidal y el carbón activado se mantuvo con agitación moderada durante 12 horas. Trascurrido este tiempo, el color rosado de la disolución coloidal desapareció, indicando que las nanopartículas de oro habían desaparecido de la disolución. A continuación, la mezcla se secó a 50 °C hasta la completa evaporación del disolvente.

El contenido en oro de los catalizadores Au/CA preparados se cuantificó mediante espectrometría de masas con plasma de acoplamiento inductivo (ICP-MS) y fue confirmado por fluorescencia de rayos X por reflexión total (TXRF). La distribución del tamaño de partícula se halló a partir del análisis de las imágenes obtenidas por microscopía de trasmisión electrónica (TEM). Los resultados mostraron que el tamaño de las nanopartículas protegidas por ácido tánico (de 5, 7 ó 10 nm de diámetro) soportadas sobre el carbón activado no se alteró durante el método de preparación, y su contenido en oro se ajustó al esperado. Sin embargo, el catalizador obtenido a partir de la disolución coloidal de nanopartículas protegidas por citrato sódico, mostró un contenido en oro significativamente inferior al esperado (0,13%), y el tamaño de partícula se modificó ligeramente durante la síntesis, obteniéndose una distribución bimodal, centrada en 3,2 y 5,7 nm. La distribución de especies de oro superficial de todos los catalizadores empleados en este estudio, Au/TiO_2, Au/Fe_2O_3 y Au/CA, se determinó mediante espectroscopía fotoelectrónica de rayos X (XPS). Se detectaron las especies Au^0 and Au^+ en todos los catalizadores, siendo Au^0 la especie mayoritaria en Au/TiO_2 y Au/CA (79 and 70%, respectivamente), y Au^+ en Au/Fe_2O_3 (74%).

Los experimentos de oxidación húmeda con peróxido de hidrógeno se llevaron a cabo en discontinuo, en un reactor de vidrio con un condensador de reflujo. El reactor se cargó con 45 mL de una disolución de fenol o alcohol benzílico (5 g/L) a pH=3,5 con 0,125 g de catalizador. Una vez alcanzada la temperatura de trabajo, 80 °C, se alimentaron 5 mL de una disolución de peróxido de hidrógeno de la concentración necesaria para la mineralización de fenol o alcohol benzílico. Con el fin de seguir la evolución de la reacción se tomaron muestras periódicamente y se analizaron mediante diferentes técnicas. Los compuestos orgánicos implicados en

las reacciones de oxidación fueron identificados y cuantificados mediante cromatografía de líquidos de alta resolución (HPLC) y cromatografía iónica (IC). El carbón orgánico total se midió con un analizador de TOC, y la concentración de peróxido de hidrógeno se determinó a partir de un método colorimétrico ($TiOSO_4$, espectrofotómetro, λ=210 nm). Los resultados experimentales se analizaron a partir de los perfiles de conversión de los contaminantes y de COT con el tiempo de reacción, el cálculo de las velocidades iniciales y de TOF (*turnover frequency*) de las reacciones de oxidación, mineralización y descomposición de peróxido de hidrógeno. Se dio especial relevancia a la eficiencia en el consumo de especie oxidante (η_{H2O2}), determinada por la relación entre las conversiones de COT y H_2O_2.

En primer lugar se estudió el comportamiento catalítico de nanopartículas de oro de pequeño tamaño (3 nm) inmovilizadas en diferentes soportes: óxido de titanio (TiO_2), óxido de hierro (Fe_2O_3) y carbón activado (CA) en la oxidación húmeda de fenol con peróxido de hidrógeno, obteniéndose que la actividad del oro estaba fuertemente afectada por la naturaleza del soporte. La presencia de oro promovió la descomposición de peróxido de hidrógeno en todos los casos, pero los grados de oxidación y mineralización alcanzados difirieron en gran medida dependiendo del sólido sobre el que se encontró inmovilizado. Cabe destacar la ausencia de oro en todos los efluentes de reacción, lo que confirma la alta resistencia de este metal hacia la lixiviación en las condiciones de operación de estos procesos.

El catalizador Au/TiO_2 (comercial, 0,8% Au) condujo a una rápida descomposición de peróxido de hidrógeno (95% a las 4 h), debida, exclusivamente, a la presencia de oro, ya que el soporte es inerte en la reacción estudiada. Sin embargo, las conversiones de fenol y COT no superaron el 25%, lo que fue indicativo de un consumo

ineficiente de especie oxidante (η_{H2O2}≈0,2). La mayor descomposición de peróxido de hidrógeno, así como de degradación de fenol (X_{H2O2}=98%, X_{fenol}=88%, X_{COT}=40%) se obtuvo en presencia de Au/Fe_2O_3 (comercial, 4,48% Au). En este caso no fue posible conocer la actividad intrínseca del oro, ya que quedó enmascarada por la importante contribución homogénea del hierro lixiviado del propio soporte ($Fe_{lixiviado}$=73% a las 24 h de reacción). Debido a su baja estabilidad, este catalizador, fue descartado para su aplicación en procesos CWPO.

El catalizador Au/CA (preparado por impregnación, 0,13% Au), resultó el más adecuado. Permitió alcanzar conversiones intermedias de fenol y COT (X_{fenol}=63%, X_{COT}=42%, 4 h), con adecuadas eficiencias en el consumo de peróxido de hidrógeno (η_{H2O2}≈0,85). Comparando los valores de TOF (mol de substrato/mol de oro expuesto·h) correspondientes a los catalizadores Au/TiO_2 y Au/CA, se determinó que las nanopartículas de oro son más activas cuando se encuentran inmovilizadas sobre el carbón activado, a pesar de presentar en este último una distribución más amplia de tamaño de partícula y un menor contenido en especies de oro cero valente, consideradas las de mayor actividad. Además, teniendo en cuenta las velocidades iniciales de desaparición de peróxido de hidrógeno en presencia de los catalizadores Au/TiO_2, Au/CA y del soporte CA (material activo en la reacción estudiada), se observó un efecto sinérgico entre el oro y carbón. Dicho efecto fue justificado a partir de las propiedades particulares de este soporte, como su elevada capacidad de adsorción. El carbón activado promueve la adsorción de fenol sobre las proximidades de las nanopartículas de oro, disminuyendo, por un lado, la velocidad de generación de especies radicalarias mediante la ocupación parcial de los centros activos y, por otro, aumentando la probabilidad de reacción entre los radicales formados y las moléculas de fenol. Todo ello condujo a un mayor aprove-

chamiento de peróxido de hidrógeno y, por tanto, mayores grados de oxidación y mineralización. Por ello, desde el punto de vista de la actividad y eficiencia de las nanopartículas de oro, se recomendó su inmovilización sobre soportes con una importante capacidad de adsorción.

A partir de estos resultados, se propuso un mecanismo de reacción para la oxidación húmeda de fenol con peróxido de hidrógeno en presencia de Au/CA. En este mecanismo se consideró una primera etapa de adsorción de fenol sobre la superficie del carbón activado y en la interfase oro-carbón, así como la adsorción de H_2O_2 en dicha interfase, una posterior de generación de especies radicalarias sobre la superficie de las nanopartículas de oro (y sobre la superficie carbonosa), y una última etapa de reacción entre los radicales en la superficie del catalizador y liberados a la fase líquida, y las moléculas de fenol adsorbidas y disueltas el medio de reacción, respectivamente.

A continuación, se estudió el efecto del tamaño de partícula de oro en la actividad catalítica del Au/CA en la oxidación de fenol. Para ello se prepararon catalizadores de oro sobre carbón activado (Merck ref.: 102514) con distinto tamaño de partícula: 3 (distribución bimodal 3,2-5,7 nm), 5 (4,9±1,0 nm), 7 (6,8±1,7 nm) y 9 (9,1±1,1 nm) nm. Se determinó que las reacciones involucradas en el proceso de oxidación dependían en gran medida del tamaño de partícula de oro. En general, cuanto menor fue el tamaño de partícula, mayor fue el valor de TOF. Esto fue particularmente evidente en la reacción de descomposición de peróxido de hidrógeno.

Así mismo, se evaluó el efecto de la naturaleza del contaminante. Con este fin se trataron, mediante oxidación húmeda con peróxido de hidrógeno en presencia

del catalizador Au/TiO_2, dos compuestos orgánicos de diferente naturaleza: fenol, compuesto modelo típico escogido en este tipo de estudios, y alcohol bencílico, compuesto modelo más estudiado para evaluar la actividad del oro en procesos de oxidación selectiva; determinándose que el mecanismo de reacción variaba en función del contaminante tratado. En el caso del alcohol bencílico, se formó un complejo intermedio, oro-alcohol, que provocó la desaparición del alcohol incluso en ausencia de peróxido de hidrógeno. Gracias a la elevada afinidad de este compuesto por el oro, se alcanzaron mayores rendimientos en su oxidación que en la de fenol, aunque no así en la mineralización.

Una vez entendida la actividad catalítica del oro y el mecanismo de reacción cuando se encuentra inmovilizado sobre carbón activado, se llevó a cabo un estudio de condiciones de operación de la oxidación húmeda de fenol con catalizadores Au/CA, con el fin de conocer aquellas condiciones de trabajo convenientes, que aseguren una elevada eficiencia en el consumo de peróxido de hidrógeno. En este estudio se empleó un catalizador comercial Au/CA (World Gold Council), con un contenido en Au del 0,8% y un tamaño medio de nanopartícula de 10 nm, preparado por el método de coprecipitación. Las variables consideradas y los intervalos estudiados fueron los siguientes:

pH: 3,5 – 10,5

Temperatura: 50 – 80 °C

Concentración de catalizador: 0 – 6 g/L

Concentración inicial de fenol: 0,1 – 5 g/L

Dosis de peróxido de hidrógeno: 4 – 100% de la cantidad estequiométrica para la mineralización de fenol.

Los resultados de este estudio mostraron que la variable que más afectaba a la eficiencia en el consumo de peróxido de hidrógeno era la concentración inicial de fenol. Cuando ésta aumentaba también lo hacia la eficiencia, obteniéndose valores $\eta_{H2O2} \approx 1$ cuando se emplearon altas concentraciones de fenol (5 g/L), con un concentración de catalizador de 2,5 g/L. El empleo de menores concentraciones de fenol conlleva una menor cobertura de la superficie del catalizador y, por tanto, un elevado número de centros activos (nanopartículas de oro y, sobre todo, planos basales del carbón) disponibles para llevar a cabo la descomposición de peróxido de hidrógeno, generando una alta concentración de radicales en superficie, los cuales se consumen mayoritariamente en reacciones parásitas en lugar de reaccionar con fenol.

$$\cdot OH + \cdot OOH \rightarrow O_2 + H_2O$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2$$

$$\cdot OOH + \cdot OOH \rightarrow O_2 + H_2O_2$$

Debido a ello y, con el fin de garantizar un consumo eficiente de peróxido de hidrógeno, el uso de los catalizadores Au/CA sólo es recomendable para el tratamiento de aguas residuales con una carga orgánica relativamente alta: concentración de fenol

dentro del rango 1-5 g/L y relaciones másicas contaminante/catalizador superiores a 0,4. El pH no es una variable determinante, pudiendo trabajar en un amplio intervalo, comprendido entre 3,5 y 7,5. Se determinó que es necesario emplear la dosis estequiométrica de peróxido de hidrógeno y que un aumento de temperatura conduce a importantes mejoras en la oxidación de fenol. En las condiciones óptimas de operación (C_{fenol}=5 g/L, C_{H2O2}=25 g/L, T=80 °C) se alcanza la completa eliminación de contaminante y una reducción del COT del 70%, a las 22 h de reacción.

Tras la investigación centrada en la actividad y eficiencia del catalizador Au/CA, se llevó a cabo un estudio sobre su estabilidad y posible reutilización, en el cual el catalizador fue sometido a varios ciclos de reacción de 24 h cada uno. Se observó una importante pérdida de actividad del primer al segundo ciclo, debido a la adsorción de ácidos orgánicos sobre la superficie de las nanopartículas de oro, manteniéndose prácticamente constante en usos sucesivos. La actividad de este catalizador fue fácilmente recuperada mediante un tratamiento térmico a temperatura relativamente baja (200 °C).

Los productos de oxidación formados en la oxidación húmeda de fenol con peróxido de hidrógeno en presencia de Au/CA fueron compuestos aromáticos (resorcinol, hidroquinona y ***p***-benzoquinona) y ácidos carboxílicos (maleico, malónico, acético, oxálico y fórmico). Los valores de COT calculados a partir de los productos de reacción identificados fueron muy próximos a los medidos (diferencias inferiores al 15%), poniendo de manifiesto la ausencia de compuestos de condensación no identificados, verdadero problema en otros procesos de oxidación avanzada. La presencia del oro modificó la selectividad respecto al carbón activado cuando éste se emplea como catalizador. Esto fue explicado a partir de la diferente orientación de las moléculas de fenol cuando son adsorbidas sobre las nanopartículas de oro

con respecto a cuando lo hacen sobre la superficie de carbón activado. La molécula de fenol se adsorbe sobre el oro a través del átomo de oxígeno, adquiriendo una orientación vertical, mientras que sobre la superficie del carbón lo hace a través de los anillos aromáticos del mismo, dando lugar a una orientación horizontal del fenol. De este modo, en presencia del oro se favorece la hidroxilación de fenol en las posiciones meta y para (formación de resorcinol e hidroquinona, respectivamente) e inhibe la hidroxilación en la posición orto (catecol). Así mismo, la presencia de oro permitió una oxidación más rápida de los compuestos aromáticos y un mayor grado de mineralización.

Una vez establecida la ruta de oxidación de fenol con el catalizador Au/CA, se propuso un esquema de esquema de reacción simplificado:

$$H_2O_2 + Au^0 \rightarrow \cdot OH + OH^- + Au^+$$

$$H_2O_2 + Au^+ \rightarrow \cdot OOH + H^+ + Au^0$$

$$Fenol + \cdot OH + \cdot OOH \rightarrow Aromáticos + Ácidos + CO_2 + HO_2$$

A partir de los resultados obtenidos en el estudio de las variables de operación, anteriormente comentado y, considerando la desactivación del catalizador Au/CA con el tiempo de reacción, se obtuvo el siguiente modelo cinético (en ausencia de limitaciones difusionales) para la descomposición de peróxido de hidrógeno y la oxidación de fenol, válido en un amplio intervalo de pH (3,5 - 7,5), lo que representa una importante ventaja frente al proceso homogéneo.

$$r_{H2O2}\left(\frac{g_{H2O2}}{L\cdot h}\right) = [5447 \pm 2{,}58\ (h^{-1})]\cdot e^{\frac{-30330\pm2660\left(\frac{J}{mol}\right)}{R\cdot T}} \cdot e^{-k_{d,H2O2}(h^{-1})\cdot t(h)} \cdot C_{H2O2}\left(\frac{g_{PH2O2}}{L}\right)$$

$$r_{Fenol}\left(\frac{g_{Fenol}}{L\cdot h}\right) = [61635 \pm 34\left(\frac{L}{g_{Fenol\cdot h}}\right)]\cdot e^{\frac{-45781\pm9145\left(\frac{J}{mol}\right)}{R\cdot T}} \cdot e^{-k_{d,Fenol}(h^{-1})\cdot t(h)} \cdot C_{Fenol}^{2}\left(\frac{g_{Fenol}}{L}\right)^{2}$$

Concluyendo, se ha encontrado un nuevo catalizador, activo y eficiente, para la oxidación húmeda de fenol con peróxido de hidrógeno: nanopartículas de oro soportadas sobre carbón activado. Este catalizador consigue superar las principales limitaciones de los catalizadores heterogéneos empleados en procesos de oxidación húmeda, evita la lixiviación de la fase activa y promueve un consumo eficiente de peróxido de hidrógeno; además permite trabajar con aguas residuales en un amplio intervalo de pH (3,5 -7,5). Sin embargo, para obtener la eliminación completa de contaminante se requieren elevados tiempos de reacción, cercanos a las 24 h, cuando se emplean temperaturas de 80 °C. Además, es necesario trabajar en ciclos de reacción y regeneración, ya que el catalizador se desactiva con el uso debido al ensuciamiento de la superficie del oro por la adsorción de ácidos orgánicos (intermedios típicos en la oxidación húmeda de contaminantes orgánicos). La ventaja que presenta este catalizador frente a otros encontrados en la bibliografía es que es posible restablecer su actividad catalítica. No obstante, esto no resulta suficiente para hacer del oro un catalizador idóneo para procesos CWPO, motivo por el cual se impulsó a la búsqueda de catalizadores más económicos, sin fase metálica, como los materiales carbonosos.

Nuestro interés en los materiales carbonosos como catalizadores para procesos de oxidación húmeda con peróxido de hidrógeno radica, por un lado, en el hecho de que no requieren de una fase activa que catalice la descomposición de peróxido de hidrógeno, de este modo se evitan los problemas tan habituales de lixiviación y, por lo tanto, de desactivación por este fenómeno; y por otro, en su bajo coste y alta disponibilidad. Los materiales carbonosos catalizan la descomposición de peróxido de hidrógeno a través de un mecanismo redox superficial de transferencia electrónica, dando lugar a la formación de especies radicalarias ($^{\cdot}OH$ y $^{\cdot}OOH$), que oxidan los contaminantes orgánicos en disolución o adsorbidos sobre la superficie del mismo.

Se ha trabajado con tres tipos de materiales carbonosos con propiedades muy diferentes: dos carbones activados (CA-Merck, ref.: 102514 y CA-Panreac, ref.: 3108L), dos negros de humo (NH-Chemviron, ref.: 2156090 y NH-Vulcan, ref.: CC72R) y dos grafitos (G-Sigma-Aldrich, ref.: 282863 y G-Fluka, ref.: 1249167), con el objetivo de estudiar su posible aplicación como catalizadores en procesos de oxidación húmeda con peróxido de hidrógeno. Estos materiales fueron caracterizados mediante difracción de rayos X (DRX), isotermas de adsorción/desorción de N_2, análisis elemental (AE), fluorescencia de rayos X por reflexión total (TXRF), desorción térmica programada (TPD) y termogravimetría (TGA), con el fin de conocer sus propiedades físico-químicas. Los carbones activados, son materiales amorfos, con una desarrollada estructura porosa y un contenido significativo de grupos superficiales oxigenados (GSO). Por su parte, los grafitos exhibieron propiedades contrarias; se trata de materiales cristalinos, con bajo desarrollo superficial y escaso contenido en GSO, mientras que los negros de humo presentaron propiedades intermedias entre los dos anteriores. El contenido en cenizas fue relativamente bajo para todos los materiales, excepto para CA-Merck, con un 4% y el G-Sigma-Aldrich, con un

0,5%. En este último caso, dichas cenizas están constituidas mayoritariamente por hierro (≈90%).

Aunque la actividad de los materiales carbonosos en la reacción de descomposición de peróxido de hidrógeno es ampliamente conocida, la predicción de la misma es compleja, ya que depende de sus propiedades físico-químicas. Obtener una información precisa sobre dichas propiedades requiere, habitualmente, del empleo de numerosas técnicas de caracterización: análisis termogravimétrico (TGA), difracción de rayos X (DRX), desorción térmica programada (TPD), oxidación térmica programada (TPO), espectroscopía fotoelectrónica de rayos X (XPS), espectrometría de masas con plasma de acoplamiento inductivo (ICP-MS), espectroscopía de infrarrojos por transformada de Fourier (FTIR), isotermas de adsorción/desorción de N_2 (S_{BET}), etc. Esta técnicas implican, generalmente, largos tiempos de análisis y costes elevados. A pesar de ello, en muchos casos no son concluyentes ya que, las propiedades físico-químicas de los materiales carbonosos presentan, en muchos casos, efectos cruzados y acoplados entre sí. En este escenario, el desarrollo de una técnica de caracterización rápida, económica y sencilla, que permita predecir la actividad de estos materiales en la reacción de descomposición de peróxido de hidrógeno, y así poder seleccionar potenciales catalizadores para el proceso CWPO, es un desafío atractivo. En este trabajo se ha propuesto el empleo de una técnica de caracterización electroquímica: la voltametría cíclica (VC). La validación de esta técnica se realizó comparando los resultados obtenidos en la caracterización electroquímica de cada uno de los carbones en presencia de peróxido de hidrógeno con los resultados de actividad hallados cuando fueron empleados como catalizadores en la reacción de descomposición de este reactivo.

En este estudio, se han empleado tres tipos de materiales carbonosos con propiedades muy diferentes, dos carbones activados (CA-Merck y CA-Panreac), dos negros de humo (NH-Chemviron y NH-Vulcan) y dos grafitos (G-Sigma-Aldrich y G-Fluka). Además, CA-Merck y G-Sigma-Aldrich fueron sometidos a un lavado con una disolución concentrada de HCl (CA-Merck-HCl y G-Sigma-Aldrich-HCl) con el fin de reducir su contenido en metales y poder evaluar así, el efecto de esta propiedad en la reacción de descomposición de peróxido de hidrógeno. Por su parte, la influencia de los grupos superficiales oxigenados se estudió trabajando con el carbón CA-Panreac fresco y lavado con ácido nítrico (CA-Panreac-HNO_3), tratamiento gracias al cual, se incrementó su contenido en GSO en gran medida.

El dispositivo experimental empleado para llevar a cabo las medidas electroquímicas consistió en una celda convencional de tres electrodos: electrodo de trabajo (carbón vítreo), electrodo auxiliar (Au) y electrodo de referencia (Ag/AgCl). El carbón se depositó sobre el electrodo trabajo en forma de tinta, una vez que se consiguió una suspensión homogénea del mismo (6 mg de material carbonoso se dispersaron en 730 μL de agua milli-Q mediante agitación ultrasónica). Las condiciones de operación de dichos experimentos fueron las siguientes: pH=3,5 (HCl), T=25 °C, velocidad de barrido=10 mV/s y rango de potencial comprendido entre -0,6 y 1 V. En primer lugar se determinó la capacidad culómbica (CC) de los materiales carbonosos realizando una voltametría cíclica de los mismos en ausencia de peróxido de hidrógeno. Este parámetro (calculado como el área del voltagrama obtenido) resultó ser proporcional a la superficie específica (medida como área BET) de los carbones. Cuanto mayor es la superficie especifica, mayor es el número de centros activos en el carbón (zonas ricas en electrones), lo que implica una mayor carga culómbica. Este hecho abrió la puerta al empleo de la VC como técnica para

determinar, de forma aproximada, la superficie específica de los materiales carbonosos.

Posteriormente, con el fin de analizar el comportamiento electroquímico de estos materiales en presencia de peróxido de hidrógeno (especie electroactiva), se realizaron ensayos adicionales en presencia de una disolución concentrada de este reactivo (C_{H2O2}=25 g/L). Cuando el material carbonoso y el peróxido de hidrógeno se pusieron en contacto, se midió el potencial en circuito abierto (E_{ocp}), el cual se corresponde con un potencial mixto y se encuentra, para todos los carbones, dentro del rango de los potenciales de reducción y oxidación de peróxido de hidrógeno (-0,905 y 1,566 V respectivamente, Ag/AgCl). Comparando los voltagramas obtenidos en ausencia y presencia de peróxido de hidrógeno, se determinaron los potenciales a los cuales comienzan las reacciones de reducción y oxidación de peróxido de hidrógeno (E_{onset}) y, a partir de la representación del sobrepotencial aplicado (E-E_{ocp}) frente al logaritmo de la intensidad de corriente (I), se determinaron las pendientes de Tafel (b) y la corriente de intercambio del proceso (i_o). Todos estos parámetros son indicativos de la actividad exhibida por los materiales carbonosos en la reacción de descomposición de peróxido de hidrógeno. El análisis de los mismos dio una idea de la complejidad de las etapas involucradas en dicha reacción, en las que se incluyen etapas de adsorción, desorción y transferencia de carga.

Tras analizar los distintos parámetros electroquímicos (E_{ocp}, E_{onset}, b, i_o) con la constante cinética aparente de cada carbón, determinada en la reacción de descomposición de peróxido de hidrógeno, llevada a cabo en un reactor de vidrio a 80 °C, pH=3,5, $C_{catalizador}$=2,5 g/L y C_{H2O2}=25 g/L, se obtuvo que la corriente de intercambio del proceso fue el parámetro más concluyente, ya que es indicativo del pro-

ceso global (reducción y oxidación de peróxido de hidrógeno), encontrándose una relación lineal entre éste y la constante cinética aparente de descomposición de peróxido de hidrógeno (k_d, cinética de pseudo-primer orden) en todos los casos estudiados. Mediante estos resultados, se demostró que la voltametría cíclica es una técnica sencilla, rápida y concluyente para la predicción de la actividad catalítica de los materiales carbonosos en la reacción de descomposición de peróxido de hidrógeno, conclusión que podría hacerse extensible a otro tipo de reacciones redox.

La caracterización electroquímica de los carbones modificados químicamente (CA-Merck-HCl, G-Sigma-Aldrich-HCl, CA-Panreac-HNO_3) permitió además discriminar la influencia de las propiedades físico-químicas en la actividad catalítica de dichos materiales en la reacción de descomposición de peróxido de hidrógeno. Así, los resultados obtenidos indicaron que la característica más determinante en la actividad de un carbón es su contenido en metales, en particular el hierro, seguido de la superficie específica y, por último, el contenido en grupos superficiales oxigenados. Por tanto, el orden de actividad que se obtuvo fue el siguiente: CA-Merck > G-Sigma-Aldrich > CA-Merck-HCl > CA-Panreac > NH-Vulcan > CA-Panreac-HNO_3 > G-Sigma-Aldrich-HCl > NH-Chemviron > G-Fluka.

Por otro lado, esta técnica electroquímica permitió conocer de forma más exhaustiva el comportamiento catalítico de los materiales carbonosos en la descomposición de peróxido de hidrógeno, determinando que la etapa limitante de este proceso es la regeneración de los centros activos del carbón (oxidación de peróxido de hidrógeno a radicales hidroperóxido a partir de la reducción del carbón). Además, se ha comprobado que fenol y peróxido de hidrógeno compiten por los mismos centros activos de la superficie carbonosa y que la ac-

tividad de los centros activos disponibles tras la adsorción de fenol permanece invariable.

Una vez demostrada la actividad de carbones activados, negros de humo y grafitos en la descomposición de peróxido de hidrógeno, se pueden considerar como catalizadores potenciales en procesos de oxidación húmeda con peróxido de hidrógeno. Así, se procedió al estudio de su actividad catalítica, eficiencia en el consumo de peróxido de hidrógeno y estabilidad en la reacción de oxidación húmeda de fenol con dicho oxidante. Los experimentos se realizaron en la misma instalación experimental empleada para el estudio de los catalizadores basados en nanopartículas de oro (reactor de vidrio en discontinuo). Del mismo modo, la evaluación de las reacciones de oxidación se siguió mediante las técnicas de análisis anteriormente descritas (HPLC, IC, TOC, colorimetría).

La evaluación de la actividad catalítica de los carbones activados, los materiales carbonosos más empleados en procesos CWPO, no es fácil debido a la importante contribución que tiene el fenómeno de adsorción. Por otro lado, la eficiencia en el consumo de peróxido de hidrógeno, factor clave para la economía del proceso y para alcanzar adecuados grados de oxidación y mineralización, suele ser baja, ya que parte de los radicales formados sobre la superficie del carbón se recombinan entre sí (reacciones parasitas), consumiéndose el peróxido de hidrógeno sin oxidar la materia orgánica.

Por tanto, el éxito de estos materiales como catalizadores en el proceso CWPO depende de poder inhibir o minimizar la extensión de estas reacciones improductivas de recombinación radicalaria y mantener una alta selectividad hacia

la reacción de oxidación entre el contaminante orgánico y los radicales hidroxilo e hidroperóxido.

Con el fin de aumentar la eficiencia en el consumo de peróxido de hidrógeno, los trabajos encontrados en bibliografía suelen orientarse hacia la modificación de carbones activados mediante tratamientos químicos para incrementar el contenido y/o modificar la naturaleza de los grupos superficiales oxigenados. En el presente estudio, sin embargo, se ha puesto atención a la modificación de la superficie especifica del carbón, propiedad más determinante en la actividad catalítica de estos materiales que los grupos superficiales oxigenados (demostrado previamente mediante voltametría cíclica). Esta modificación consistió en reducir la superficie específica del carbón activado mediante su recubrimiento con el propio compuesto orgánico a tratar. Para ello, se ensayó el tratamiento de aguas residuales de mayor carga orgánica que las habitualmente empleadas en el proceso CWPO, pero todavía dentro del intervalo de Demanda Química de Oxígeno recomendado para la aplicación de este tipo de tratamientos (DQO<20 g/L). Así, en la oxidación de fenol con peróxido de hidrógeno, sólo cuando se emplearon concentraciones de fenol relativamente elevadas (≈5 g/L, en lugar de los valores típicos 10-100 mg/L) y una alta relación másica fenol/carbón activado ($C_{fenol}/C_{carbón}$=2, superior a las comúnmente empleadas, en torno a 0,2), se mantuvo un consumo eficiente de la especie oxidante (η=0,9-1), a 80 °C. Bajo estas condiciones de operación (C_{fenol}=5 g/L, $C_{fenol}/C_{carbón}$=2, C_{H2O2}=5 g/L, pH=3,5, 80 °C) se alcanzó la completa eliminación del contaminante (>97%) y un alto grado de mineralización (70%) tras 24 h de reacción. De modo contrario a lo que cabe esperar con otros catalizadores, una reducción de la superficie específica de los carbones activados y, en consecuencia, de la

actividad del catalizador en la reacción de descomposición de peróxido de hidrógeno, fue beneficiosa para el rendimiento global del proceso de oxidación, ya que condujo a una mayor selectividad hacia las reacciones de oxidación y mineralización de la materia orgánica. De este modo, gran parte de la superficie carbonosa se encuentra ocupada por moléculas de fenol adsorbidas, con lo que la descomposición de peróxido de hidrógeno y, por tanto, la formación de radicales hidroxilo e hidroperóxido se produce de una forma más progresiva, concentrándose una menor cantidad de especies radicalarias en la superficie del carbón, minimizando así su recombinación. Por otro lado, las moléculas de fenol, al estar adsorbidas sobre los planos basales del carbón, se encuentran muy accesibles a las especies oxidantes formadas sobre esta misma superficie. Ambos factores contribuyen a aumentar la probabilidad de reacción entre los radicales ($^{\cdot}OH$, $^{\cdot}OOH$) y las moléculas de fenol.

Por tanto, para que los carbones activados sean catalizadores activos y eficientes en el proceso CWPO, es necesario trabajar con aguas contaminadas por compuestos orgánicos que muestren alta afinidad por el carbón activado, con elevadas relaciones contaminante/carbón y altas concentraciones de materia orgánica; además, con el fin de aumentar la velocidad de oxidación y mineralización es necesario el empleo de temperaturas en torno a 80 °C. Como consecuencia de las condiciones de operación empleadas (altas cargas de contaminante y relaciones contaminante/carbón), el fenómeno de adsorción presenta una baja contribución en la desaparición de fenol.

Durante la reacción de oxidación de fenol con H_2O_2, la superficie de los carbones activados tiende a homogeneizarse (adquiriendo similares propiedades

físico-químicas), y por tanto, la actividad catalítica exhibida por los mismos, también. Así, carbones activados con diferentes propiedades físico-químicas iniciales, como CA-Merck y CA-Panreac (desarrollo superficial, contenido en cenizas, contenido en GSO), no presentaron diferencias en su actividad a tiempos largos de reacción (24 h).

El estudio de estabilidad y reutilización de carbones activados mostró la progresiva desactivación de los mismos con el número de ciclos de reacción, de 24 h cada uno. La velocidad de descomposición de peróxido de hidrógeno disminuyó paulatinamente como consecuencia de la presencia de depósitos carbonosos, en particular productos de condensación, que se detectaron adsorbidos sobre la superficie carbonosa mediante análisis termogravimetrico de los catalizadores usados. Dichos depósitos, bloquearon el acceso a los microporos, provocando una importante disminución de la superficie específica de los carbones, así como un aumento en la funcionalización de los mismos; se incrementó especialmente su contenido en grupos carboxílicos, lactonas y anhídridos. La actividad de estos materiales pudo ser restablecida gracias a la recuperación de sus propiedades texturales y electroquímicas, tras ser sometidos a un tratamiento térmico a 350 °C en atmósfera de aire. Dicha temperatura fue elegida considerando la temperatura a la que tiene lugar la combustión de los productos carbonosos adsorbidos (300-350 °C), determinada mediante TGA.

Estos resultados fueron extensibles a otros materiales, que sin ser carbones activados, presentaron una capacidad de adsorción también elevada, como el NH-Vulcan (S_{BET}≈240 m^2/g). Los resultados obtenidos con este material en la oxidación de fenol con peróxido de hidrógeno fueron algo peores que en el caso de los car-

bones activados, de acuerdo a su menor capacidad para descomponer el peróxido de hidrógeno, como consecuencia de su menor superficie específica y ausencia de metales. La desactivación sufrida por este material fue más acusada que para los carbones activados, debido a la pérdida completa de microporosidad, por lo que su empleo, frente al de los carbones activados, no reporta ninguna ventaja.

De este modo, es de esperar que materiales carbonosos con bajo desarrollo superficial y, por tanto, con menor capacidad de adsorción, como el negro de humo Chemviron, y los grafitos Sigma-Aldrich y Fluka, presenten una menor tendencia a la desactivación por deposición de materia carbonosa sobre su superficie durante los procesos de oxidación húmeda. Los ensayos de actividad de estos catalizadores en la de oxidación de fenol (C_{fenol}=1 g/L, C_{H2O2}=5 g/L, C_{cat}= 2,5 g/L pH=3,5, 80 °C) mostraron el mismo orden de actividad que el obtenido en la descomposición de peróxido de peróxido de hidrógeno: G-Sigma-Aldrich > NH-Chemviron> G-Fluka. Así, en presencia del catalizador G-Sigma-Aldrich se obtuvieron mayores conversiones (X_{fenol}=98% y X_{COT}=60%) que con NH-Chemviron (X_{fenol}=60% y X_{COT}=35%, a las 4 h de reacción), aunque eficiencias en el consumo de peróxido de hidrógeno menores (η_{H2O2}=68% *vs.* η_{H2O2}=92%). G-Fluka fue descartado para su empleo como catalizador por la baja actividad exhibida, como consecuencia de su baja superficie específica y ausencia de cenizas. La mayor actividad exhibida por G-Sigma-Aldrich, similar a la que presentan los catalizadores homogéneos, fue atribuida, en parte, a la contribución del hierro en disolución, procedente de la lixiviación de Fe de las cenizas del grafito. Esta lixiviación fue consecuencia de la presencia de una importante concentración de ácido oxálico como intermedio de la oxidación de fenol, el cual forma un complejo con el hierro (oxalato de hierro). Debido a ello, el catalizador mostró una acusada

pérdida de actividad del primer al segundo uso (la conversión de fenol a las 4 h de reacción disminuyó del 98% al 45%).

Por el contrario, el negro de humo CB-Chemviron, resultó ser estable durante cinco ciclos consecutivos de reacción, de 24 h cada ciclo, manteniendo una eficiencia en el consumo de peróxido de hidrógeno, superior a η=0,9. No sufrió desactivación debido a la ausencia de depósitos carbonosos sobre su superficie, corroborado mediante la comparación de los termogramas obtenidos de los catalizadores frescos y usados. Además, las velocidades iniciales de descomposición de peróxido de hidrógeno y de oxidación y mineralización de fenol en presencia de este carbón, aumentaron en torno a un 20% del primer al segundo ciclo, manteniéndose constantes en el resto de usos. Esta sobre-actividad fue explicada atendiendo al aumento del contenido de grupos superficiales oxigenados que experimentó el carbón tras la reacción, y que provocó una ligera disminución de la superficie especifica del mismo. La creación de grupos ácidos, tipo carboxílicos, anhídridos, éteres y fenólicos, confirió al material un mayor carácter hidrofílico, permitiendo una mayor difusión de los reactivos hacia los centros activos del material, mejorando así su actividad catalítica.

Por lo tanto, tras el estudio realizado se pudo concluir que NH-Chemviron es un catalizador activo, eficiente y estable en la oxidación húmeda de fenol con peróxido de hidrógeno y, por tanto, se trata de un catalizador prometedor para el tratamiento de aguas residuales industriales mediante procesos CWPO. La actividad catalítica resultó ser algo inferior a la presentada por los carbones activados y los catalizadores Au/CA, ya que tras 24 h de reacción, se alcanzaron conversiones de fenol y COT del 75% y 40%, respectivamente (1 g/L, T=80 °C, C_{cat}=2,5 g/L). Con el fin de

aumentar dicha actividad, se estudió el efecto de la carga de catalizador, entre 0 y 7,5 g/L, la temperatura de reacción, 80 y 90 °C, y el pH inicial, 3,5 y 6 (manteniendo en todos los casos una concentración inicial de fenol de 1 g/L y la dosis de peróxido de hidrógeno estequiométrica para su mineralización). Los resultados mostraron un efecto positivo de la carga de catalizador y de la temperatura de reacción en el grado de oxidación y mineralización de fenol; además, ambos factores afectaron también positivamente a la eficiencia en el consumo de peróxido de hidrógeno, que fue η=1 a altas concentraciones de catalizador y temperaturas elevadas. Por otro lado, el pH inicial de las aguas no parece ser una variable determinante en presencia de este material, ya que se obtuvieron idénticos resultados a las 24 h de reacción trabajando con un pH inicial de 3,5 y 6, lo que representa una importante ventaja de cara a su aplicación industrial. En las condiciones de operación seleccionadas (C_{fenol}=1 g/L, C_{H2O2}=5 g/L, C_{cat}= 5 g/L, pH=3,5, 90 °C), se alcanzó la eliminación total de fenol y una reducción de COT del 70% a tiempos de reacción de 16 h, con una eficiencia máxima en el consumo de peróxido de hidrógeno. Por tanto, la actividad exhibida por este catalizador y, sobre todo, la eficiencia en el consumo de especie oxidante, son muy elevadas en comparación con los valores recogidos en la literatura en el empleo de otros materiales carbonosos como catalizadores de estos procesos (en ningún caso se han utilizado negros de humo).

Durante el estudio dedicado a la oxidación húmeda de fenol con peróxido de hidrógeno con distintos catalizadores basados en materiales carbonosos, los resultados se evaluaron no solo en términos de conversión de fenol, COT y peróxido de hidrógeno, sino que también se identificaron y cuantificaron los intermedios de oxidación. A partir de éstos se propuso un esquema de reacción en serie-paralelo para la oxidación húmeda de fenol con sólidos carbonosos como catalizadores. En

presencia de estos materiales, el fenol puede ser oxidado selectivamente en las posiciones *meta*, *orto* o *para*, dando lugar a la formación de catecol, resorcinol e hidroquinona (este último en equilibrio con *para*-benzoquinona), respectivamente, o bien de manera no selectiva, generando ácido maleico, malónico, acético, oxálico y fórmico directamente, como así demuestra la presencia de estos compuestos desde los primeros momentos de reacción. Lo intermedios aromáticos son oxidados a su vez, dando lugar a ácidos carboxílicos. La formación de resorcinol (compuesto no detectado en el proceso catalítico homogéneo) es característica de la presencia de un material carbonoso, lo que indica que la oxidación de fenol tiene lugar sobre la superficie del catalizador, además de producirse también en la fase líquida, gracias a las especies radicalarias desprendidas a dicha fase (detectadas mediante el test de azul de metileno). Por otro lado, los valores de COT calculado a partir de los compuestos identificados es bastante próximo al medido experimentalmente (diferencias<10%), lo que es indicativo de la ausencia de productos de condensación, típicamente formados en la oxidación de compuestos aromáticos mediante el proceso Fenton. Debido a las diferentes propiedades físico-químicas de los materiales carbonosos empleados, que afectan en particular a la capacidad de adsorción de éstos, se observaron diferentes selectividades de reacción, así en presencia de CB-Chemviron, la concentración de compuestos aromáticos es mayor y requieren de más tiempo para oxidarse, debido a que se adsorben en menor medida sobre la superficie carbonosa y, por tanto, no se produce su condensación.

Con el fin de estudiar la versatilidad y aplicación de los materiales carbonosos en los tratamientos de oxidación húmeda con peróxido de hidrógeno, se ha trabajado con un agua residual industrial procedente de la industria vitivinícola. La problemática particular de este tipo de aguas residuales reside en su alto carácter esta-

cional, que conduce a elevadas fluctuaciones, tanto en la cantidad, como en la calidad de los efluentes generados a lo largo del año, y en la presencia de compuestos recalcitrantes y no biodegradables (polifenoles), lo que dificulta en muchos casos, su tratamiento en un sistema biológico convencional. Las aguas residuales que se emplearon en este estudio proceden de una bodega localizada en Badajoz, y se caracterizan por su elevada carga orgánica, DQO≈35 g/L y COT≈11 g/L, color marrón y olor desagradable. Tras el empleo de una amplio espectro de técnicas analíticas (HPLC, IC, MASAS, etc.), tan sólo pudo identificarse el 43% de su contenido en materia orgánica. Ésta se correspondió en su mayor parte con ácidos orgánicos (principalmente ácido acético, glicólico y malónico), polifenoles y trazas de algunos compuestos alcohólicos.

Antes de tratar las aguas residuales mediante el proceso de oxidación húmeda con peróxido de hidrógeno, se realizó un estudio previo sobre la conveniencia de dicho tratamiento, ya que la elevada concentración de materia orgánica obligaría a un consumo elevado de especie oxidante, con el consecuente encarecimiento del proceso. En primer lugar, las aguas residuales fueron sometidas a distintos tratamientos físicos, como la adsorción con carbón activado o la precipitación con $Ca(OH)_2$. Estos tratamientos no resultaron efectivos, ya que la reducción de materia orgánica en ambos casos fue inferior al 15%. A continuación se procedió al tratamiento de las mismas mediante distintos procesos de oxidación húmeda con aire, proceso más apropiado que la oxidación con peróxido de hidrógeno, dado el elevado valor de DQO de las aguas (>20 g/L). Así se ensayó la oxidación húmeda catalítica con aire (en presencia de distintos materiales carbonosos: CA-Panreac, NH-Chemviron, G-Sigma-Aldrich a 160 °C, 10 atm, C_{cat}= 5 g/L) y no catalítica, y este mismo proceso empleando peróxido

de hidrógeno como promotor (160 °C, 10 atm, C_{cat}= 0 ó 5 g/L, C_{H2O2}=20% de la cantidad estequiométrica correspondiente a la DQO inicial).

Estos ensayos de oxidación se llevaron a cabo en un reactor de teflón cubierto por una camisa de acero inoxidable con control de presión y temperatura, introduciendo en continuo un caudal de gas (O_2 o N_2) de 92 NmL/min. Se tomaron muestras a distintos tiempos de reacción y se analizaron mediante las técnicas anteriormente descritas (COT, IC y H_2O_2). En este caso se determinó también la DQO y el contenido en compuestos fenólicos mediante métodos colorimétricos (ISO 6060 y test *folin*, respectivamente).

Los resultados mostraron que sólo la adición de peróxido de hidrógeno como promotor condujo a un incremento en la oxidación de materia orgánica (X_{DQO}=40% en el proceso no catalítico y 55-60% en el catalítico). Esa actividad fue debida exclusivamente a la reacción de oxidación de la materia orgánica con especies radicalarias procedentes de la descomposición de peróxido de hidrógeno, ya que las conversiones de DQO y COT obtenidas en este mismo ensayo cuando se trabajó con N_2 en lugar de O_2, fueron equivalentes. Estos resultados fueron explicados de acuerdo a la naturaleza de dichas aguas, constituidas en gran parte por ácidos orgánicos, compuestos refractarios a los tratamientos de oxidación húmeda con aire.

El empleo de mayores concentraciones de peróxido de hidrógeno, como la correspondiente a la cantidad estequiométrica con respecto a la DQO inicial del agua residual, en el tratamiento CWPO con el catalizador G-Sigma-Aldrich, permitió obtener conversiones de DQO y COT superiores a las obtenidas en el tratamiento de oxidación húmeda con H_2O_2 como promotor, a pesar de operar a una tempe-

ratura significativamente menor (80 *vs.* 160 °C). La mayor actividad catalítica exhibida por el grafito frente al negro de humo y el carbón activado, es consistente con su mayor capacidad para descomponer el peróxido de hidrógeno (como fue previamente determinado mediante voltametría cíclica), debido a su contenido en Fe (0,44%). Análisis de TXRF del efluente de reacción y del catalizador recuperado tras la misma, mostraron una nula lixiviación de hierro (a diferencia de lo que ocurre cuando este material cataliza la oxidación de fenol), mostrando una adecuada estabilidad durante los tres ciclos consecutivos de reacción ensayados.

Estos resultados indicaron que el tratamiento de aguas vitivinícolas mediante procesos CWPO en presencia de un material grafítico, con trazas de hierro en su estructura, podría ser una solución interesante, siempre y cuando permitiera asimilar importantes fluctuaciones de carga orgánica, típicas en este tipo de aguas residuales, de modo que la misma unidad de oxidación pudiera ser empleada para el tratamiento de cualquier efluente generado durante el año, ajustando únicamente la dosis de peróxido de hidrógeno. Para estudiar este efecto se varió la concentración inicial de materia orgánica en un amplio intervalo (de 3,5 a 35 g/L DQO, empleando la cantidad estequiométrica de peróxido de hidrógeno para cada caso, a T=100 °C, pH=3,8, P=0,7 MPa y C_{cat}=5 g/L), y se observó que esta modificación no afectaba al rendimiento del proceso, obteniéndose idénticos perfiles de conversión de DQO para todos los casos estudiados. Este aspecto supone una importante ventaja desde el punto de vista operacional, en comparación con los procesos de oxidación biológica, en los que habría que adaptar los microorganismos a las necesidades puntuales, o incorporar un tanque de acumulación y homogeneización previo al tratamiento, de modo que la concentración de materia orgánica que se introdujera al reactor biológico se mantuviera siempre en unos niveles concretos.

Por último, se llevó a cabo un estudio de la influencia de las condiciones de operación del proceso, con el fin de minimizar el consumo de peróxido de hidrógeno, asegurando la obtención de efluentes no ecotoxicos y potencialmente biodegradables. Así, se estudió el efecto de la temperatura de reacción (80–125 °C), el pH inicial (2,2-7), la concentración de peróxido de hidrógeno (0–160%) y el modo de dosificar dicha especie (en una única dosis al inicio de la reacción o repartida en varias dosis). Los mejores resultados, $X_{DQO,COT}$=80%, $X_{polifenoles}$=100%, η_{H2O2}=85%, eliminación total del color y el olor, y efluentes carentes de ecotoxicidad, se obtuvieron trabajando a 125 °C, pH bruto de las aguas (3,8) y empleando la cantidad estequiométrica de peróxido de hidrógeno adicionada en varias etapas, en un tiempo de reacción de 4 h. El hecho de no alcanzar conversiones de DQO superiores al 80%, bajo ninguna de las condiciones de operación empeladas, es debido a la existencia de una fracción orgánica refractaria a la oxidación, constituida principalmente por ácido acético, cuya oxidación implicaría operar a temperaturas muy superiores a las aquí empleadas.

Por lo tanto, se puede concluir que el empleo de materiales carbonosos con bajo desarrollo superficial, como algunos negros de humo, y grafitos con contenido en Fe, son catalizadores adecuados para procesos CWPO. Aunque presentan menores actividades que sales de hierro empleadas en el proceso Fenton, son ventajosos, ya que pueden dar solución a muchos de los problemas asociados a dicho tratamiento, como reutilizar el catalizador, no generar lodos de hidróxido de hierro, maximizar la eficiencia en el consumo de peróxido de hidrógeno y poder operar en un mayor intervalo de pH. Resulta complicado generalizar sobre su actividad y estabilidad, ya que ambas dependen en gran medida del efluente a tratar, por lo que se requiere de estudios específicos en función de la naturaleza del agua residual que permitan encontrar las condiciones óptimas de trabajo para cada carbón.

The use of heterogeneous catalysts for the treatment of industrial wastewater containing persistent organic pollutants by catalytic wet peroxide oxidation (CWPO process) is expected to overcome the main drawbacks associated with the use of homogeneous catalysts in Fenton process (typically salts of Fe^{2+}), which are the continuous loss of the dissolved catalyst and the need to separate it from the effluent, the generation and management of iron sludge generated in the neutralization step, and the need to operate in a narrow range of pH (3-4). On the other hand, the use of heterogeneous catalysts is subjected to the fact that they exhibit high activity, good stability and ensure an efficient consumption of hydrogen peroxide. In spite of the considerable research efforts in this area, progress in the development of economical catalysts in order to meet these requirements is still ongoing.

Since the main objective of this Thesis is to find an active, stable and efficient carbon based catalyst for CWPO processes, this report summarizes the results

obtained dealing with these materials. This study was carried out considering the use of carbon materials either as support or catalysts. In the former, active phases resistant to metal leaching, such as gold nanoparticles, were supported on activated carbon. In the latter, activated carbon, along with other carbon materials, such as carbon blacks and graphites were considered. The mentioned catalysts have been used in the treatment of wastewater containing model compounds, such as phenol and benzyl alcohol, and real wastewater from the wine industry.

Previous studies about the use of gold nanoparticles in CWPO processes have demonstrated that they are interesting candidates when immobilized on certain supports, *i.e.* hydroxyapatite or diamond nanoparticles. The nanosize gold particles present appropriate redox properties that, allows the decomposition of hydrogen peroxide into hydroxyl and hydroperoxyl radicals, as long as a high resistance to leaching, which is the main cause of deactivation for heterogeneous catalysts in CWPO processes.

In this work, the immobilization of gold nanoparticles on economical and more available supports than those previously studied, such as activated carbon, has been studied. With the aim of explaining some controversial results found in the few works dedicated to this catalyst in literature, the origin of the catalytic activity of gold supported nanoparticles was firstly studied by working with gold nanoparticles immobilized on different supports. Subsequently, a study about operating conditions for Au/activated carbon (Au/AC) catalyst was carried out in order to select its operational window that ensure high efficiency of hydrogen peroxide consumption in CWPO process. Finally, the stability and reusability of this catalyst were analyzed; a reaction scheme for the wet pe-

roxide oxidation of phenol proposed, and from the latter, a kinetic model was discriminated.

To study origin of the gold nanoparticles activity, commercial catalysts, Au/TiO_2 (Mintek, 0.8% Au, d_{Au}=3.1±1.8 nm) and Au/Fe_2O_3 (World Gold Council, 4.48% Au, d_{Au}=3.6±0.9 nm) and Au/AC catalysts synthesized in our laboratory by impregnation and dry method, were used. This method is based on contacting the colloidal solution of gold nanoparticles with the required amount of activated carbon (Merck, ref.: 102514) to obtain a catalyst with a final gold content of 0.5 wt%. Colloidal aqueous solutions with gold nanoparticles of different sizes were employed: 3 nm, with sodium citrate as a capping agent (supplied by Strem Chemicals Inc.) and 5, 7 and 10 nm, protected by tannic acid (supplied by Nanocomposix). The colloidal suspension with the activated carbon were stirred under moderate agitation for 12 hours. After this time, the red color of the colloidal solution faded, indicating the removal of gold from the aqueous phase. Then, the mixture was dried at 50 °C until complete evaporation of the remaining solution.

The gold content of the Au/AC catalysts was measured by mass spectrometry with inductively coupled plasma (ICP-MS) and was confirmed by X-ray fluorescence by total reflection (TXRF). The particle size distribution was determined by transmission electron microscopy (TEM). The results of the characterization analyses demonstrated that the size of the tannic acid-capped gold nanoparticles (5, 7 or 10 nm) supported on activated carbon were not altered during the preparation method, and that gold content was also adjusted to the expected value. However, the catalyst obtained from the citrate-capped gold nanoparticles suspension showed a significantly lower gold content than the expected one (0.13 wt%).

The particle size was also modified during synthesis, obtaining a bimodal distribution centered at 3.2 and 5.7 nm. The exposed gold surface species in all catalysts (Au/TiO_2, Au/Fe_2O_3 and Au/AC), were determined by X-ray photoelectron spectroscopy (XPS). Au^0 and Au^+ species were detected in all the catalysts, being Au^0 the main specie in Au/TiO_2 and Au/AC (79 and 70%, respectively) and Au^+ in Au/Fe_2O_3 (74%).

Oxidation experiments were carried out batchwise in a glass reactor with a reflux condenser. The reactor was charged with 45 mL of phenol or benzyl alcohol solution (5 g/L) at pH=3.5 with 0.125 g of catalyst. After reaching the selected temperature (80 °C), 5 ml of a hydrogen peroxide solution of the required concentration for pollutant mineralization were fed. In order to follow the reaction evolution, samples at different reaction times were taken from the reactor and immediately analyzed by different techniques. Organic compounds were identified and quantified by high performance liquid chromatography (HPLC) and ion chromatography (IC). Total organic carbon was measured with a TOC analyzer and hydrogen peroxide concentration was determined by a colorimetric method ($TiOSO_4$, spectrophotometer, λ=210 nm). The experimental results were analyzed according to pollutants and TOC conversion profiles, initial rates and TOF (turnover frequency) of the oxidation, mineralization and hydrogen peroxide decomposition reactions. Special attention was placed on the efficiency of oxidizing specie consumption (η_{H2O2}), determined by the relationship between TOC and H_2O_2 conversions.

Firstly, the catalytic performance of small gold nanoparticles (3 nm) supported on different supports: titania (TiO_2), iron oxide (Fe_2O_3) and activated carbon (AC) were studied in the CWPO of phenol, obtaining that the gold activity was strongly

affected by the nature of the support. Gold promoted the decomposition of hydrogen peroxide in all cases, but the temporal evolution of phenol and TOC conversions largely differ from one catalyst to another depending on the support. It was remarkable the absence of gold in the effluents, confirming the high resistance of this metal to leaching under the operating conditions of the process.

Au/TiO_2 catalyst (commercial, 0.8% Au) led to a rapid decomposition of hydrogen peroxide (95% at 4 h), due to the gold nanoparticles, since TiO_2 is inert in this reaction. However, phenol and TOC conversions remain lower than 25% (at 4 h), which was indicative of an inefficient consumption of the oxidizing species ($\eta_{H2O2}\approx0.2$). The highest hydrogen peroxide decomposition and phenol degradation (X_{H2O2}=98%, X_{Phenol}=88%, X_{TOC}=40%) were achieved with Au/Fe_2O_3 (commercial, 4.48% Au). However, in this case, the intrinsic activity of gold was masked by the significant contribution of the iron leached from the support ($Fe_{leached}$=73% at 24 h of reaction). Due to the poor stability of this catalyst, Au/Fe_2O_3 was discarded for its application in CWPO processes.

Au/AC (prepared by impregnation-dry method, 0.13% Au), was the most appropriate catalyst. It allowed to reach intermediate values of phenol and TOC conversions (X_{Phenol}=63%, X_{TOC}=42%, 4 h), with acceptable efficiencies in the consumption of hydrogen peroxide ($\eta_{H2O2}\approx0.85$). Comparing the activity of Au/TiO_2 and Au/AC in terms of TOF (mol substrate/mol exposed gold·h) it was evidenced that gold nanoparticles supported on activated carbon are more active than on titania, in spite of presenting a wider particle size distribution and having a lower content of zero valent gold species, being those the most active sites. Furthermore, considering the values of the initial rates of hydrogen peroxide disappearance in the presence of Au/TiO_2, Au/AC

and AC (support active in this reaction), a synergistic effect between carbon and gold was observed. This effect was justified considering the high adsorption capacity of this support. Activated carbon promotes the phenol adsorption on the vicinity of gold nanoparticles; thus, the production rate of radical species by partial occupation of the active sites slow down and by this way a more efficient use of hydrogen peroxide is obtained, resulting in higher oxidation and mineralization degrees. Therefore, from the point of view of the activity and efficiency of gold nanoparticles, their immobilization on supports with good adsorption capacity was recommended.

Considering these results, a reaction mechanism for the wet peroxide oxidation of phenol in the presence of Au/AC was proposed. This mechanism considered a first step of phenol adsorption on the carbon surface and the gold-carbon interface, as well as hydrogen peroxide adsorption mainly on that interface, a second step, in which the generation of radical species on the gold nanoparticles (and on the carbon surface) takes place, and a final step consisting in the reaction between radical species, on the carbon surface and released into the liquid phase, and phenol, adsorbed and dissolved in the reaction media, respectively.

Next, the effect of gold particle size on the catalytic activity of Au/AC in the oxidation of phenol was studied. For this purpose, size-selected gold nanoparticles of 3 (bimodal distribution from 3.2 to 5.7 nm), 5 (4.9 ± 1.0 nm), 7 (6.8 ± 1.7 nm) and 9 (9.1 ± 1.1 nm) nm were deposited on activated carbon (Merck ref.: 102514). The results show that the reactions involved in the oxidation process (decomposition of hydrogen peroxide, phenol oxidation and mineralization) were highly dependent on the gold particle size. In general, the lower the particle size, the higher the TOF values. This fact was particularly evident in hydrogen peroxide decomposition reaction.

Lastly, the effect of the nature of the pollutant on the CWPO performance with gold was evaluated. For this purpose, two organic compounds: phenol, typical model compound chosen in these studies, and benzyl alcohol, typical model compound chosen to assess the gold activity in selective oxidation reactions in liquid phase, were treated by wet peroxide oxidation in the presence of Au/TiO_2 catalyst, concluding that the reaction mechanism varied depending on the pollutant nature. In the case of benzyl alcohol, with significant affinity towards gold, a gold-alcohol complex is formed, which results in the disappearance of the alcohol even in the absence of the oxidant. Therefore, higher yields were achieved in the oxidation of benzyl alcohol than phenol, though the same was not observed in the mineralization.

Once the catalytic activity of Au/AC was understood and a reaction mechanism proposed, a study of the operating conditions in the CWPO of phenol was carried out in order to know the treatment conditions in which a high efficiency of hydrogen peroxide consumption is assured. In this study, an Au/AC commercial catalyst (World Gold Council) with a gold content of 0.8 wt% and an average particle size of 10 nm, prepared by the co-precipitation method, was used. The variables and their range of values considered one were the following:

- pH: 3.5 – 10.5
- Temperature: 50 – 80 °C
- Catalyst concentration: 0 – 6 g/L
- Initial phenol concentration: 0.1 – 5 g/L
- Hydrogen peroxide dose: 4 – 100% of the stoichiometric amount for phenol mineralization.

The results demonstrated that the most determinant variable affecting the efficiency of hydrogen peroxide consumption was the initial phenol concentration. The higher initial phenol concentration the higher conversions under otherwise identical conditions. Thus, at phenol concentrations equal to 5 g/L and catalyst load of 2.5 g/L, efficiency values equal to one, $\eta_{H2O2}\approx1$, were reached. Working at low phenol initial concentrations, there is a lower occupancy of the surface active sites (gold nanoparticle interface and carbon basal planes) or increase of those available for hydrogen peroxide decomposition, and it is possible to produce high concentrations of radicals which are consumed in parasitic reactions instead of reacting with phenol.

$$\cdot OH + \cdot OOH \rightarrow O_2 + H_2O$$

$$\cdot OH + \cdot OH \rightarrow H_2O_2$$

$$\cdot OOH + \cdot OOH \rightarrow O_2 + H_2O_2$$

Therefore, the use of Au/AC catalyst is only recommended for the treatment of high organic bearing-wastewater, which in the case of phenol, implies initial concentrations of phenol around 5 g/L and pollutant/catalyst mass ratios greater than 0.4. With respect to the effect of other operating conditions of the oxidation process on the efficiency of Au/AC catalyst resulted that pH was not a key variable, and it was possible to operate in a wide pH range, from 3.5 to 7.5. However, it was necessary to employ the stoichiometric dose of hydrogen peroxide and high temperatures to achieve high oxidation and mineralization degrees. Under the operating condition selected (C_{Phenol}=5 g/L, C_{H2O2}=25 g/L,

T=80 °C) total phenol removal and TOC reduction of 70% at 22 h of reaction time were reached.

After the investigation focused on the activity and efficiency of Au/AC catalysts, a stability and reusability study was carried out by subjecting the catalyst at several reaction cycles of 24 h each. A significant decrease in the catalytic activity from the first to the second cycle was observed caused by the poisoning due to carboxylic acids adsorption onto the gold surface, intermediates arising from phenol oxidation. The activity of this catalyst was easily recovered by a relatively low temperature heat treatment (200 °C).

The oxidation by-products formed in the CWPO of phenol in the presence of Au/AC were aromatic compounds (resorcinol, hydroquinone and ***p***-benzoquinone) and carboxylic acids (maleic, malonic, acetic, oxalic and formic). The TOC values calculated from the identified reaction products were very close to those measured (difference less than 15%), showing the absence of unidentified species such as condensation compounds, which represents a real problem in other advanced oxidation processes. The presence of gold modified the selectivity of activated carbon when used as catalyst. This fact was explained by the different orientation of phenol molecules on gold nanoparticles and on carbon surface. Phenol is predominantly attached to gold by the oxygen atom, whereas the attachment on carbon occurs by the aromatic ring. Thus, a vertical orientation to the surface and a parallel one are, respectively, expected. In the former, the attack of radicals to the ***orto*** position can be hindered and then catechol formation inhibited, whereas in the latter the accessibility of the ***orto*** position is similar to the others. In addition, the

presence of gold led to a more rapid oxidation of aromatics compounds and higher mineralization degrees.

Once phenol oxidation route in the presence of Au/AC catalyst was determined, a simplified reaction scheme was proposed:

$$H_2O_2 + Au^0 \rightarrow \cdot OH + OH^- + Au^+$$

$$H_2O_2 + Au^+ \rightarrow \cdot OOH + H^+ + Au^0$$

$$Phenol + \cdot OH + \cdot OOH \rightarrow Aromatics + Acids + CO_2 + HO_2$$

Considering the results obtained from the operating variable study and the catalyst deactivation upon reaction time, the following kinetic model (in the absence of diffusional limitations) was elucidated for the decomposition of hydrogen peroxide and the removal of phenol, valid over a wide range of pH (3.5 to 7.5). This last aspect represents an important advantage over the homogeneous process.

$$r_{H2O2}\left(\frac{g_{H2O2}}{L \cdot h}\right) = [5{,}447 \pm 2.58\ (h^{-1})] \cdot e^{\frac{-30{,}330 \pm 2{,}660\left(\frac{J}{mol}\right)}{R \cdot T}} \cdot e^{-k_{d,H2O2}(h^{-1}) \cdot t(h)} \cdot C_{H2O2}\left(\frac{g_{PH2O2}}{L}\right)$$

$$r_{Ph}\left(\frac{g_{Ph}}{L \cdot h}\right) = 61{,}635 \pm 34\ \left(\frac{L}{g_{Ph \cdot h}}\right) \cdot e^{\frac{-45{,}781 \pm 9{,}145\left(\frac{J}{mol}\right)}{R \cdot T}} \cdot e^{-k_{d,Ph}(h^{-1}) \cdot t(h)} \cdot C_{Ph}^2\left(\frac{g_{Ph}}{L}\right)^2$$

In conclusion, a new catalyst, active and efficient for the CWPO of phenol has been found, Au/AC. This catalyst overcomes the main limitations of the heterogeneous catalysts, since prevents leaching of gold and allows efficient consumption of hydrogen peroxide. Moreover, it can be used in a wide range of wastewater pH

(3.5 -7.5). However, long reaction times (closed to 24 h) are required to achieve complete phenol removal, at 80 °C. Furthermore, Au/AC is deactivated upon use due to gold poisoning by adsorption of organic acids (typical intermediates in CWPO processes) but this deactivation is totally reversible. Therefore, it is necessary to operate with this catalyst under reaction-regeneration cycles. This disadvantage has prompted us to search for catalysts without metallic phase, such as carbon materials.

Our interest in carbon materials as catalysts for CWPO processes lies, firstly, on its activity to catalyze the decomposition of hydrogen peroxide without incorporation of a metallic phase, therefore, the deactivation by the leaching phenomenon is avoided, and secondly, on the economical cost and high availability of these materials. Carbon materials catalyze the mentioned reaction through an electron transfer mechanism, resulting in the formation of radical species (·OH and ·OOH), which oxidize the organic pollutants in solution or adsorbed onto the carbon surface.

Three types of carbon materials with different properties have been used in this study: two activated carbons (AC-Merck, ref.: 102514 and AC-Panreac, ref.: 3108L), two carbon blacks (CB-Chemviron, ref.: 2156090 and CB-Vulcan, ref.: CC72R) and two graphites (G-Sigma-Aldrich, ref.: 282863 and G-Fluka, ref.: 1249167). In order to know about their physico-chemical properties, these materials were analyzed by X ray diffraction (XRD), N_2 adsorption/desorption, elemental analysis (EA), total X-ray reflection fluorescence (TXRF), programmed thermal desorption (TPD) and thermogravimetric analysis (TGA). Activated carbons are amorphous materials with a developed porous structure and significant amounts of surface oxygen

groups (SOG). Graphites exhibited opposite properties; they are almost crystalline materials with a very low specific surface area and scarce SOG, while carbon blacks presented structural, textural and chemical features between the two. The ash content was relatively low for all materials, except for AC-Merck, with 4wt% and G-Sigma-Aldrich, with 0.5wt% (being Fe the 90% of those).

Though the activity of carbon materials in hydrogen peroxide decomposition reaction is well known, its prediction is not straightforward. The physico-chemical features affect the electron-transfer reactivity and, consequently, the carbon activity. A high number of tedious, time-consuming and expensive characterization techniques: thermogravimetric analysis (TGA), X-ray diffraction (XRD), thermal programmed desorption (TPD), temperature programmed oxidation (TPO), X ray photoelectron spectroscopy (XPS), mass spectrometry with inductively coupled plasma (ICP-MS), Fourier transform infrared (FTIR), adsorption/desorption of N_2, etc. are required in order to characterize the carbons. In spite of this, achieving conclusive results is not always possibly. The reason is that the different physico-chemical properties cannot be analyzed independently due to the difficulty of tailoring a single carbon characteristic upon the preparation process, without affecting the rest. Therefore, the occurrence of coupled effects is common and makes impracticable a reasonable prediction of the catalyst activity of carbon materials as function of their characteristics. In this scenario, the development of a rapid, inexpensive and simple characterization technique for predicting the activity of these materials in the hydrogen peroxide decomposition reaction, and thereby allowing us to select those materials with catalytic potential for CWPO, is an attractive challenge. In this work, the use of an electrochemical characterization technique, cyclic voltammetry (CV), has been proposed. The validation of this technique was

performed by comparing the results obtained in their electrochemical characterization, in the presence of hydrogen peroxide, against those obtained when they were used as catalysts in the decomposition of this reagent.

As commented above, we have employed with three types of carbon materials with different characteristics, two activated carbons (AC-Merck and AC-Panreac) two carbon blacks (CB-Chemviron and CB-Vulcan) and two graphites (G-Sigma-Aldrich and G-Fluka). Furthermore, CA-Merck and G-Sigma-Aldrich were washed with concentrated HCl aqueous solution (AC-Merck-HCl and G-Sigma-Aldrich-HCl) in order to reduce their content of metals and, by this way, evaluate the effect of this property in the catalytic activity. Also, the influence of SOGs was evaluated by using fresh AC-Panreac and its homologous treated with nitric acid (AC-Panreac-HNO_3) in order to increase the amount of SOGs.

Electrochemical measurements were carried out in a conventional three-electrode cell: working electrode (glassy carbon), counter electrode (Au) and reference electrode (Ag/AgCl). The carbon sample was deposited on the working electrode as an ink (10 μL; 6 mg of carbon material was dispersed in 730 μL of milli-Q water by ultrasonic agitation). The operating conditions of these experiments were as follows: pH=3.5 (HCl), T=25 °C, scan rate=10 mV/s and potential range from -0.6 to 1 V. Firstly, the working electrode was subjected to cyclic voltammetry in the absence of hydrogen peroxide, obtaining the coulombic charge (CC). This parameter (calculated as the area of the voltammogram) was proportional to the specific surface area (measured by BET area) of the carbon tested. The higher the specific surface the larger the number of active sites on the carbon surface (electron-rich areas), which implies a higher coulombic charge. This finding opens the door to the

use of CV as characterization technique to determine the surface area of carbon materials.

Subsequently, in order to examine the electrochemical performance of these materials in the presence of hydrogen peroxide (electroactive specie), additional tests were conducted with this reagent (C_{H2O2}=25 g/L). When carbon materials and hydrogen peroxide were put in contact, the open circuit potential (E_{ocp}) was measured. This value corresponds to a mixed potential, being within the thermodynamic reduction/oxidation potentials of hydrogen peroxide (-0.905 and 1.566 V respectively, Ag/AgCl). Comparing the voltammograms obtained in the absence and the presence of hydrogen peroxide, the potentials at which begin the oxidation and reduction reactions of hydrogen peroxide (Eonset) are determined. Finally, the Tafel slope (b) and the exchange current (i_o) were calculated from the representation of the applied overpotential ($E-E_{ocp}$) ***vs.*** the logarithm of the current intensity (I). All these parameters were indicative of the activity of the different carbon materials in the hydrogen peroxide decomposition. Their analyses revealed the complexity of the reaction, which involves several steps, such as adsorption, desorption and charge transfer.

According to the analyses of the different electrochemical parameters (E_{ocp}, E_{onset}, b, i_o) with the apparent first-order rate constant, determined in the reaction experiments ($C_{catalyst}$=2.5 g/L, C_{H2O2}=25 g/L, 80 °C and pH=3.5) carried out for each carbon, the exchange current (i_0) was the most conclusive parameter, since takes into account the overall process (reduction and oxidation of hydrogen peroxide reactions). A linear relationship between both parameters (i_0, k_d) was found for all the solids. Therefore, it was demonstrated that cyclic voltammetry is a rapid,

direct, and conclusive technique for predicting the catalytic activity of carbon materials for hydrogen peroxide decomposition, conclusion that can be extended to other redox reactions.

The electrochemical characterization of the chemically modified carbons (AC-Merck-HCl, G-Sigma-Aldrich-HCl, AC-Panreac-HNO_3) provided an understanding of the effects of the different physico-chemical properties on their catalytic activity for the hydrogen peroxide decomposition reaction. Thus, the results indicated that the content of metals, particularly iron, followed by the specific surface area and, finally, the content of surface oxygen groups are the mayor factors influencing the exchange current value of the carbons and, therefore, their catalytic activity. Therefore, the activity order obtained was the following: AC-Merck> G-Sigma-Aldrich> AC-Merck-HCl> AC-Panreac> CB-Vulcan> AC-Panreac-HNO_3> G-Sigma-Aldrich-HCl > CB-Chemviron > G-Fluka.

Cyclic voltammetry also enables an insight into the reaction mechanism. It has been demonstrated that the limiting step in hydrogen peroxide decomposition is the regeneration of the active sites upon carbon reduction; phenol and hydrogen peroxide compete for the same active sites of the carbon surface and, also, the activity of the available sites remains unaltered upon reaction.

Once the activity of activated carbons, carbon blacks and graphites in the decomposition of hydrogen peroxide was demonstrated, these materials can be considered as potential catalysts in wet peroxide oxidation processes. Thus, we proceeded to study their catalytic activity, efficiency, stability and reusability in the CWPO of phenol. The experiments were performed in the same experimental device as pre-

viously described (glass batch reactor). Likewise, the oxidation reactions were followed by the above mentioned analytical techniques (HPLC, IC, TOC, colorimetry).

The evaluation of the catalytic activity of activated carbon, the most used carbon materials in CWPO processes, is difficult due to the important contribution of the adsorption phenomenon to the total pollutant uptake. Moreover, the efficiency in the consumption of hydrogen peroxide, which is crucial for the cost-effectiveness of the process and to achieve adequate oxidation and mineralization degrees, is usually low, since the majority amount of the radicals formed on the carbon surface are consumed in parasitic reactions.

Therefore, the success of these materials as catalysts in CWPO depends on their ability to inhibit or minimize the extension of parasitic reactions in order to maintain a high selectivity towards the oxidation reaction between radical species and organic pollutants.

With the aim of increasing the efficiency of hydrogen peroxide consumption, papers in literature usually deal with the chemical modification of activated carbons to increase the content and/or modify the nature of the surface oxygen groups. In contrast, we proposed in this study the modification of the specific surface area, a determinant property for the catalytic activity of these materials, as previously demonstrated by cyclic voltammetry. This modification consisted on reducing the carbon surface area by its covering with the organic pollutant. For this purpose, the treatment of high loaded wastewater was tested, but still within the range of chemical oxygen demand (COD) recommended for the implementation of this type of treatment (COD<20 g/L). Thus, in the CWPO of phenol, only when rela-

tively initial high concentrations (5 g/L phenol, instead of the typical values 10-100 mg/L) and a high phenol/activated carbon mass ratios (***viz***. C_{phenol}/C_{carbon}=2, instead of the commonly employed around 0.2) were used, an efficient consumption of the oxidant specie was maintained (η_{H2O2}=0.9-1 at 80 °C). Under these operating conditions (C_{phenol}=5 g/L, C_{phenol}/C_{carbon}=2, C_{H2O2}=5 g/L, pH=3.5, 80 °C) complete removal of the pollutant (> 97%) and high mineralization degree (70%) were achieved after 24 h. Contrary to the behavior expected with other catalysts, a reduction of the carbon specific surface area, and consequently, of its catalytic activity, was beneficial to the overall oxidation process because it resulted in a higher selectivity towards oxidation and mineralization of the organic pollutant. The reason is that most of the carbon surface is occupied by adsorbed phenol molecules, so that the decomposition of hydrogen peroxide and, therefore, the formation of radical species, take place in a more progressive way, minimizing their recombination. Furthermore, phenol molecules, adsorbed on the carbon basal planes, are very accessible to the oxidizing species, also formed on the same active sites. Both factors, the slowdown of the decomposition reaction rate and the presence of phenol in the vicinity, contribute to increase the probability of reaction between these radicals (·OH, ·OOH) and phenol molecules.

To sum up, in order to assure an efficient consumption of hydrogen peroxide dealing with activated carbons catalysts in CWPO process, it is necessary to work with wastewater containing organic compounds with affinity towards activated carbons, employing high pollutant/carbon mass ratios and also high concentrations of organic matter. With the aim to increase the oxidation and mineralization rates, temperatures around 80 °C are requiered. At these operating conditions, the adsorption phenomenon has low contribution in the disappearance of phenol.

Upon wet peroxide oxidation, the activated carbon surface was modified, the specific surface area reduced and the amount of SOGs increased, and in general, the differences in the initial physico-chemical properties were reduced so that, activated carbons with initially different physico-chemical properties, such as AC-Merck and AC-Panreac, did not show significant differences in activity at long reaction times (24 h).

The stability and reusability study of activated carbons showed their progressive deactivation with the number of reaction cycles, of 24 h each. The hydrogen peroxide decomposition rate gradually decreased upon cycles due to the presence of carbonaceous deposits, identified as condensation by-products adsorbed on the carbon surface (detected by TGA). These deposits blocked the access to the micropores, causing a significant decrease of the specific surface area, as well as, an enhancement of the carbon fictionalization (carboxyl, anhydride and lactone groups were increased). The activity of activated carbons was completely restored by recovering their textural and electrochemical properties with a thermal treatment at 350 °C, in air atmosphere. This temperature was selected considering the temperature at which the combustion of the adsorbed carbonaceous products took place (300-350 °C), according to the profiles obtained by TGA.

The results obtained for activated carbons were extended to other porous materials with high adsorption capacity, such as CB-Vulcan (S_{BET}≈240 m^2/g). Its catalytic activity in the CWPO of phenol was somewhat lower than those exhibited by the activated carbons, consequently to its lower ability to decompose hydrogen peroxide, because of its lower specific surface area and absence of metals. The deactivation suffered was higher than that experimented by activated carbons, since the

complete loss of microporosity takes place. Therefore, the use of these materials, compared with the activated carbons, does not report any advantage.

According to the above results, it is expected that non-porous carbon materials or carbon materials with low surface development and, therefore, low adsorption capacity, such as CB-Chemviron, G-Sigma-Aldrich and G-Fluka, are high resistant to deactivation by deposition of carbonaceous material. Activity assays of these catalysts in the CWPO of phenol (C_{Phenol}=1 g/L, C_{H2O2}=5 g/L, C_{cat}= 2.5 g/L pH=3.5, 80 °C) showed the same activity order than that obtained in the decomposition of hydrogen peroxide (by CV): G-Sigma-Aldrich > CB-Chemviron > G-Fluka. In the presence of G-Sigma-Aldrich higher conversions (X_{phenol}=98% and X_{TOC}=60%) than with CB-Chemviron (X_{Phenol}=60% and X_{TOC}=35%, at 4 h) were obtained, though lower efficiencies in hydrogen peroxide consumption (η_{H2O2}=68% ***vs.*** η_{H2O2}=92%). G-Fluka was discarded because the low activity exhibited, due to its low surface area and absence of ashes. The higher activity exhibited by G-Sigma-Aldrich, similar to that presented by homogeneous catalysts, was attributed to the important contribution to the reaction of the iron detected in the reactor effluent and leached from the graphite ashes. The leaching was explained by the presence of oxidation by-products, such as oxalic acid, susceptible of forming an Fe-complex. As a result, this G-Sigma-Aldrich catalyst showed a marked loss of activity from the first to second use (phenol conversion decreased from 98% to 45% after 4 h of reaction)

On the contrary, CB-Chemviron was stable during five consecutive reaction cycles, each cycle of 24 h, maintaining the efficiency of hydrogen peroxide consumption around η_{H2O2}=0.9. This carbon did not suffer deactivation upon time on stream due to the absence of carbonaceous deposits on its surface, corroborated by TGA anal-

yses of the fresh and spent catalyst. Far from being deactivated, the initial rates of hydrogen peroxide decomposition and phenol oxidation and mineralization reactions were increased by 20% approximately from the first to the second cycle, remaining constant in successive runs. This over-activity was explained taking into account that surface oxygen groups were created upon reaction and these groups, carboxylic, anhydrides, phenolic and ethers type, though slight decrease the specific surface area, confer to the carbon with a more hydrophilic character, allowing a greater diffusion of the reagents to the active sites, which results in an enhanced catalytic activity.

Concluding, CB-Chemviron is an active, efficient and stable catalyst in the CWPO of phenol and it is a promising catalyst for the treatment of industrial wastewater. Nevertheless, the catalytic activity of this carbon (X_{phenol}=75% and X_{TOC}=40% at 24 h under 1 g/L initial phenol, T=80 °C, C_{cat}=2.5 g/L) was somewhat lower than that obtained by activated carbons and Au/AC catalysts. In order to increase the activity, the effect of catalyst loading, varied from 0 to 7.5 g/L, the reaction temperature, 80 and 90 °C, and the initial pH, 3.5 and 6, were studied (maintaining the initial phenol concentration equal to 1 g/L and using the stoichiometric dose of hydrogen peroxide for phenol mineralization in all cases). The results showed the positive effect of the catalyst loading and the reaction temperature on phenol oxidation and mineralization. Both factors also affected positively to the efficiency of hydrogen peroxide consumption, which was η_{H2O2}=1 at high catalyst concentration and high temperature. The initial wastewater pH did not appear to be an influencing variable, since the same results were obtained at pH 3.5 and 6 after 24 hours of reaction time, which, on the other hand, is an important advantage for the industrial application of CWPO with CB-Chemviron. Under the selected

operating conditions (C_{Phenol}=1 g/L, C_{H2O2}=5 g/L, C_{cat}= 5 g/L, pH=3.5, 90 °C), total elimination of phenol and TOC reduction of 70% were achieved at 16 h reaction time, with a maximum efficiency in the consumption of hydrogen peroxide. Thus, the activity exhibited by the CB-Chemviron and, particularly, the efficiency in the consumption of the oxidizing specie, are very high compared to the values reported in the literature related to the use of carbon materials as catalysts in these processes. Noteworthy, carbon blacks have been unprecedented tested for CWPO.

The results of the CWPO of phenol with the different carbon materials were evaluated not only in terms of phenol, TOC and hydrogen peroxide conversions, but also by the identification and quantification of the intermediate by-products. From these analyses, a parallel-serial reaction scheme was proposed. In the presence of carbon materials, phenol is either selectively oxidized in *meta*, *ortho* or *para* positions, leading to the formation of catechol, resorcinol and hydroquinone (being the latter in equilibrium with *para*-benzoquinone), respectively, or non-selectively oxidized yielding short chain organic acids, such as maleic, malonic, acetic, oxalic and formic acids, as supported by the presence of these carboxylic acids from the early stage of reaction. Aromatic intermediates were also further oxidized to carboxylic acids. The formation of resorcinol only takes place in the presence of carbon, indicating that the oxidation of phenol occurs on the catalyst surface, apart from in the liquid phase by the radical species released (detected by the methylene blue test). Meanwhile, TOC values calculated from the identified compounds were quite close to the measured ones (difference<10%), and thus, condensation by-products were not present in the effluent, as typically found in the Fenton process. The different physico-chemical properties of the carbon materials, which particularly affects to their adsorption capacity, gave rise to different carbon selectivity. In case

of CB-Chemviron, the concentration of aromatic compounds in the effluent was higher and longer times were required for their removal.

Finally, to complete the work presented in this Thesis, the versatility and applicability of carbon materials in CWPO were studied by the treatment of real wastewater. Wastewater from the wine industry was selected because the seasonal fluctuations of the winemaking effluents and the presence of recalcitrant and no biodegradable compounds (polyphenols) usually complicate their biological treatment. The wastewater used in this study came from a winery located in Badajoz, and were characterized by high organic load, COD≈35 g/L and TOC≈11 g/L, brown color and unpleasant odor. After using a wide spectra of analytical techniques (HPLC, IC, MASS, etc.), only 43% of their organic matter content could be identified, which accounted for by the presence of organic acids (mainly acetic, glycolic acid and malonic acids), polyphenols and trace amounts of alcoholic compounds.

Before studying the treatment of the winery wastewater by CWPO in the presence of carbon catalysts, an assessment about the advisability of this treatment was performed since the high COD loads of the water will imply high consumptions of hydrogen peroxide, which will be in detriment of the cost-effectiveness of the CWPO process. In the previous studies, the winery wastewaters were subjected to different physical treatments, such as adsorption with activated carbon or precipitation with $Ca(OH)_2$. These treatments were not effective; the organic matter reduction was below 15% in both cases. Wet air oxidation, in principle, a more appropriate process than CWPO taking into account the initial high COD value (>20 g/L) of the wastewater, was also performed. The wastewaters were treated by catalytic wet air oxidation (CWAO, in the presence of various carbon materi-

als: AC-Panreac, CB-Chemviron and G-Sigma-Aldrich, at 160 °C, 10 atm, C_{cat}=5g/L) and non-catalytic wet air oxidation (WAO, at 160 °C, 10 atm, C_{cat}=5g/L). Also, these two processes were carried out using hydrogen peroxide as promoter (PP-CWAO and PP-WAO at 160 °C, 10 atm, C_{H2O2}=20% of the stoichiometric amount corresponding to the initial COD and 0.5 g/L of catalyst or 0, respectively).

The WAO, PP-WAO, CWAO and PP-CWAO experiments tests were carried out in a stainless-steel pressure vessel (PTFE) autoclave reactor, with temperature and pressure control, with a flow-rate (O_2 or N_2) of 92 NmL/min. Samples at different reaction times were taken from the reactor and analyzed by the techniques described above (TOC, IC and H_2O_2). COD measurements were accomplished according to the standard method (ISO 6060). Polyphenolic compounds were measured by the *Folin-Reagent* test at 700 nm using a UV-VIS spectrophotometer.

The results showed that reduction of COD only took place in the presence of hydrogen peroxide (X_{COD}=40% in the PP-WAO and 55-60% in the PP-CWAO) and only this oxidant was active at the operating conditions employ since similar COD and TOC conversions were obtained by working with N_2 instead of O_2 in the PP-WAO and PP-CWAO experiments. These results were explained attending to the wastewaters nature, mainly constituted by organic acids, refractory to wet air oxidation treatments at the moderate conditions employed (160 ° and 10 atm).

The treatment of the winery wastewater by CWPO in the presence of graphite allowed higher COD and TOC reductions and at substantially lower temperature than H_2O_2-promoted CWAO (80 *vs.* 160 °C) but higher dose of hydrogen peroxide (100% ***vs.*** 20% the stoichiometric dose with respect to the initial COD). The higher

activity provided by G-Sigma-Aldrich compared to the one exhibited by activated carbon (AC-Panreac) and carbon black (CB-Chemviron) tested is consistent with the higher ability of this material to decompose hydrogen peroxide (as previously determined by cyclic voltammetry), due to the content of iron (0.44wt%). TXRF analyses of the fresh, used graphite and CWPO effluents demonstrated the absence of leached iron. In fact, the activity of G-Sigma-Aldrich was maintained upon three successive cycles.

The treatment of winery wastewaters by CWPO in the presence of a Fe-bearing graphite would be an interesting solution if this process would be capable of dealing with the typical seasonal fluctuations of organic matter concentration so that the same unit was adequate at any time just by adjusting the dose of hydrogen peroxide to the inlet organic load (COD, TOC). To study this effect, the initial concentration of organic matter was varied over a wide range (from 3.5 to 35 g/L COD, using the stoichiometric amount of hydrogen peroxide for each case at T=100 °C, pH=3.8, P=10 atm y C_{cat}=5 g/L), obtaining identical COD conversion profiles for all the studied cases. This aspect represents an important advantage from the operational point of view, compared to biological oxidation processes, in which microorganisms have to be adapted to specific needs, or incorporate a storage and homogenization tank prior to the biological treatment, with the aim of maintaining a specific level of organic matter.

Finally, in order to minimize the consumption of hydrogen peroxide and to obtain non-ecotoxic and potentially biodegradable effluents, a study about operating conditions was performed. Thus, the effect of pH (2.2 to 7), reaction temperature (80 – 125 °C), hydrogen peroxide dose (0 – 160%) and the way of feeding this reagent

(unique dose at the beginning of the reaction or stepwise addition) were investigated. The best results, $X_{COD,TOC}$=80%, $X_{polyphenols}$=100%, η_{H2O2}=85%, total removal of color and odour, and non-ecotoxic effluents, were obtained at 125 °C, raw pH of the wastewater and using the stoichiometric amount of hydrogen peroxide in stepwise addition, at 4 h. COD conversions higher than 80% were never achieved due to the existence of a refractory organic fraction to oxidation, consisting mainly of acetic acid, whose oxidation would require higher temperatures than the ones used here.

Therefore, carbon materials with low surface development, such as some carbon blacks (CB-Chemviron), and Fe-bearing graphites (G-Sigma-Aldrich), are suitable catalysts for CWPO processes. Although, their activities are lower than those exhibited by the iron salts commonly used in Fenton process, their use have important advantages, providing solutions to many of the problems associated to this treatment, such as the catalyst reusability, the absence of iron sludge, the higher efficiencies of hydrogen peroxide consumption and the wide operational pH range. However, it is difficult to generalize about the activity and stability of these non-porous carbon materials, since both aspects are highly dependent on the effluent to treat. Therefore, for each wastewater, specific studies are required in order to find the optimal operating conditions for each carbon.

6

Conclusiones/ Conclusions

De los resultados obtenidos en la presente investigación, relacionados con el empleo de catalizadores de nanopartículas de oro inmovilizadas sobre carbón activado para el tratamiento de aguas residuales industriales contaminadas por compuestos orgánicos persistentes, mediante oxidación húmeda con peróxido de hidrógeno, se extraen las siguientes conclusiones:

- La actividad y eficiencia de los catalizadores de nanopartículas de oro soportadas son dependientes de la naturaleza del soporte, del tamaño de partícula y de la afinidad del contaminante orgánico hacia el oro.

- La actividad y eficiencia son mayores cuando las nanopartículas de oro se encuentran soportadas sobre un material con elevada capacidad de adsorción, ***viz.*** carbón activado (Au/CA), de modo que se favorezca la presencia del contaminante en las proximidades de la interfase oro-soporte, donde tiene lugar,

preferentemente, la descomposición de peróxido de hidrógeno a especies radicalarias, responsables de la oxidación.

- Cuanto menor es el tamaño de las partículas de oro, mayor es su actividad. Es recomendable el empleo de nanoparticulas de diámetro igual o menor a 3 nm (TOF_{H2O2}=16,70·10^4 h^{-1}, TOF_{Fenol}=1,19·10^4 h^{-1}, TOF_{COT}=1,08·10^4 h^{-1}, para el catalizador Au/CA).

- La oxidación de contaminantes orgánicos con alta afinidad hacia el oro, como los alcoholes***, i.e.*** alcohol bencílico, que forman complejos intermedios oro-alcohol y, por tanto, compiten por los centros activos del oro con el peróxido de hidrógeno, permite un consumo más moderado y eficiente de este reactivo y, como consecuencia de ello, mayores grados de oxidación.

- La ruta de oxidación de fenol en presencia de catalizadores Au/CA indica que éste se oxida simultáneamente a compuestos aromáticos (resorcinol, hidroquinona y *para*-benzoquinona), ácidos orgánicos de cadena corta (ácido maleico, malónico, acético, oxálico y fórmico) y CO_2. Posteriormente, los compuestos aromáticos se oxidan a ácidos carboxílicos, de menor ecotoxicidad y mayor biodegradabilidad. La presencia de oro inhibe la ruta de oxidación de fenol a catecol, mientras que el empleo de un sólido carbonoso como soporte (o catalizador) promociona la ruta de oxidación de fenol a resorcinol.

- El catalizador Au/CA se desactiva debido a la adsorción de ácidos carboxílicos sobre las nanopartículas de oro. No obstante, su actividad puede ser totalmente restablecida mediante un tratamiento térmico a baja temperatura (T=200 °C).

- El estudio de la influencia de variables de operación en la oxidación húmeda de fenol con peróxido de hidrógeno con el catalizador Au/CA demuestra que para garantizar un consumo eficiente de peróxido de hidrógeno es necesario emplear relaciones másicas de contaminante/catalizador superiores a 0,4 y altas concentraciones de fenol (5 g/L).

- A partir del estudio de la influencia de variables de operación y del esquema de reacción propuesto para la oxidación húmeda de fenol con peróxido de hidrógeno en presencia de Au/CA, se ha discriminado el siguiente modelo cinético, válido para un amplio intervalo de pH (3,5 - 7,5) del agua a tratar:

$$r_{H2O2}\left(\frac{g_{H2O2}}{L\cdot h}\right) = [5447 \pm 2{,}58\ (h^{-1})]\cdot e^{\frac{-30330\pm2660\left(\frac{J}{mol}\right)}{R\cdot T}}\cdot e^{-k_{d,H2O2}(h^{-1})\cdot t(h)}\cdot C_{H2O2}\left(\frac{g_{PH2O2}}{L}\right)$$

$$r_{Fenol}\left(\frac{g_{Fenol}}{L\cdot h}\right) = [61635 \pm 34\ \left(\frac{L}{g_{Fenol}\cdot h}\right)]\cdot e^{\frac{-45781\pm9145\left(\frac{J}{mol}\right)}{R\cdot T}}\cdot e^{-k_{d,Fenol}(h^{-1})\cdot t(h)}\cdot C_{Fenol}^{2}\left(\frac{g_{Fenol}}{L}\right)^{2}$$

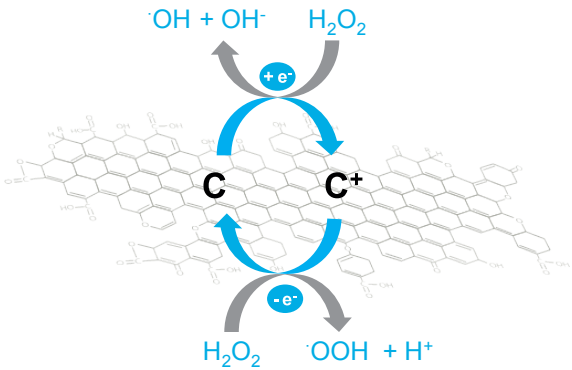
De los resultados obtenidos en la presente investigación, relacionados con el empleo de materiales carbonosos como catalizadores en el tratamiento de aguas residuales industriales contaminadas por compuesto orgánicos persistentes, mediante oxidación húmeda con peróxido de hidrógeno, se extraen las siguientes conclusiones:

- Las propiedades electroquímicas de los materiales carbonosos determinan su actividad catalítica en la reacción de descomposición de peróxido de hidrógeno. Así, la voltametría cíclica es una técnica de caracterización sencilla, rápida y eficaz que permite predecir la actividad catalítica de un amplio espectro de materiales carbonosos en dicha reacción, tales como carbones activados, negros de humo y grafitos.

- La corriente de intercambio de proceso global (i_o), determinada mediante voltametría cíclica a partir de la representación del sobrepotencial aplicado ($E-E_{ocp}$) *vs.* el logaritmo de la intensidad de corriente (I), se relaciona linealmente con la constante cinética (k_d) de la reacción de descomposición de peróxido de hidrógeno.

- El contenido en metales, especialmente en hierro, es el factor que presenta una mayor influencia en la corriente de intercambio del proceso global y, por tanto, en la actividad catalítica de los materiales carbonosos en la reacción de descomposición de peróxido de hidrógeno, seguido del desarrollo superficial (medido en términos de superficie específica) y, por último, el contenido en grupos superficiales oxigenados.

- La etapa limitante de la reacción de descomposición de peróxido de hidrógeno sobre la superficie de materiales carbonosos es la oxidación de este compuesto para dar lugar a la formación radicales hidroperóxido:



- La actividad catalítica de un material carbonoso en la oxidación húmeda de compuestos orgánicos con peróxido de hidrógeno viene determinada por su eficiencia en el consumo de la especie oxidante. Para que el catalizador de lugar a un consumo eficiente de peróxido de hidrógeno, el proceso de oxidación debe llevarse a cabo en condiciones de operación adecuadas y específicas para cada agua residual y tipo de catalizador.

- Los carbones activados y, en general, sólidos carbonosos con elevada superficie específica, son catalizadores eficientes y, por tanto, permiten alcanzar adecuados grados de oxidación y mineralización, cuando se emplean en el tratamiento de compuestos orgánicos con elevada afinidad por la superficie del carbón,

como, fenol, y, siempre y cuando, se opere con elevadas concentraciones de contaminante y altas relaciones másicas contaminante/carbón (C_{fenol}=5 g/L y relación másicafenol/carbón≈2,5, a 80 °C).

- Los carbones activados, y otros sólidos carbonosos de elevada superficie específica, se desactivan progresivamente durante la oxidación húmeda de fenol con peróxido de hidrógeno debido a la presencia productos de condensación adsorbidos sobre su superficie. Su actividad puede ser completamente recuperada mediante un tratamiento térmico a 350 °C en atmósfera oxidante.

- Los negros de humo, materiales carbonosos con un desarrollo superficial moderado y ausencia de impurezas metálicas, como el negro de humo suministrado por Chemviron (ref.: 2156090), son catalizadores activos y eficientes en procesos de oxidación húmeda con peróxido de hidrógeno (X_{fenol}=100%, X_{COT}=70%, η_{H2O2}=1, 90 °C, 16 h). Además, son catalizadores estables, ya que su capacidad de adsorción es suficientemente baja como para evitar la presencia de compuestos de condensación adsorbidos sobre su superficie.

- Los grafitos con un contenido significativo en hierro, aunque con bajo desarrollo superficial, como el suministrado por Sigma-Aldrich (ref.: 282863), son catalizadores activos y eficientes en procesos de oxidación húmeda con peróxido de hidrógeno, debido, fundamentalmente, a la actividad catalítica exhibida por el hierro (0,44%). La estabilidad y reusabilidad de estos materiales viene determinada por la resistencia del Fe a la lixiviación y, por tanto, por la naturaleza del agua residual a tratar. Así, se desaconseja su uso para el tratamiento de aguas contaminadas con compuestos orgánicos cuya oxidación de lugar a la

formación de ácido oxálico, como fenol y sus derivados. Por el contrario, son catalizadores estables en el tratamiento de otro tipo de aguas residuales, como las procedentes de la industria vitivinícola.

- El tratamiento de aguas residuales procedentes de la industria vitivinícola (DQO≈35 g/L, COT≈11 g/L, pH=3,8) mediante oxidación húmeda con peróxido de hidrógeno en presencia de un catalizador de grafito con importante contenido en hierro, ha demostrado ser una solución efectiva, ya que consigue una rápida eliminación de polifenoles, generando efluentes carentes de toxicidad. Mediante este proceso se alcanzan elevados grados de oxidación y mineralización de la materia orgánica a tiempos cortos de reacción ($X_{DQO,COT}$≈80%, 4 h a 125 °C, 10 atm, 5 g/L de catalizador, pH bruto de las aguas, y adición por pulsos de la cantidad estequiométrica de H_2O_2), y, sobre todo, es un tratamiento que permite asimilar las fluctuaciones estacionales, tanto de caudal como de concentración de materia orgánica, habituales en el agua generada en este tipo de industria.

- Los resultados obtenidos en este trabajo, que demuestran la idoneidad de los catalizadores basados en materiales carbonosos de bajo desarrollo superficial, como algunos negros de humo y grafitos, en este último caso, con contenido en Fe para contrarrestar una superficie específica demasiado pequeña, abren las puertas al empleo de otro tipo de materiales carbonosos, que aunque no sean tan económicos, ***viz.*** grafeno, óxido de grafeno, diamante, etc. posean propiedades electroquímicas adecuadas, y bajo condiciones de operación específicas a cada uno de ellos, aseguren un consumo eficiente de peróxido de hidrógeno y puedan exhibir altas actividades catalíticas en la oxidación húmeda de compuestos orgánicos, de manera que se puedan emplear en baja concentración.

The results presented in this work, related to the use of gold nanoparticles supported on activated carbon for wastewater treatment of persistent organic pollutants by catalytic wet peroxide oxidation, support the following conclusions:

- The activity and efficiency of supported gold nanoparticles are dependent on the nature of the support, the particle size and the affinity of organic pollutants towards gold.

- The activity and efficiency of gold nanoparticles are higher when they are supported on materials with high adsorption capacity, *viz.* activated carbon (Au/AC). By this way, the presence of (adsorbed) pollutants in the vicinity of the gold-support interface, where the formation of oxidant radical species mostly takes place, is enhanced.

- Gold particles with a smaller average size showed greater activity. For this reason, the use of gold nanoparticles with size of less than or equal to 3 nm is recommended (TOF_{H2O2}=16,70·10^4 h^{-1}, TOF_{Phenol}=1,19·10^4 h^{-1}, TOF_{TOC}=1,08·10^4 h^{-1}, for Au/AC catalyst).

- The oxidation of organic pollutants with good affinity towards gold, those forming intermediate complexes ***i.e.*** alcohols, results in higher oxidation degrees. The pollutant competes with hydrogen peroxide for gold active sites, which enables a slower and more efficient consumption of this oxidant.

- The phenol oxidation route in the presence of Au/AC catalysts indicates that phenol is simultaneously oxidized to aromatic compounds (resorcinol, hydroquinone and ***para***-benzoquinone), short-chain carboxylic acids (maleic, malonic, acetic, oxalic and formic acids) and CO_2. Subsequently, the aromatic compounds are oxidized to those carboxylic acids of lower ecotoxicity and higher biodegradability. The presence of gold inhibits the oxidation route of phenol to catechol, while the use of a carbon material as support (or catalyst) promotes the phenol oxidation route to resorcinol.

- Au/AC catalyst is deactivated upon CWPO by poisoning due to the carboxylic acids adsorption onto the gold surface, intermediates arising from phenol oxidation. Nevertheless, the activity can be completely restored by a low temperature heat treatment (T = 200 °C).

- The study dealing with the influence of the operating conditions on the CWPO of phenol in the presence of Au/AC demonstrates the use of contaminant/ca-

talyst mass ratios above 0.4 in order to guarantee an efficient consumption of hydrogen peroxide.

- Considering the results from the operating condition study and the proposed phenol oxidation route in the presence of Au/AC, the following kinetic model was discriminated, valid for a wide range of wastewater pH (3.5-7.5) :

$$r_{H2O2}\left(\frac{g_{H2O2}}{L\cdot h}\right) = [5{,}447 \pm 2.58\,(h^{-1})]\cdot e^{\frac{-30{,}330\pm2{,}660\left(\frac{J}{mol}\right)}{R\cdot T}}\cdot e^{-k_{d,H2O2}(h^{-1})\cdot t(h)}\cdot C_{H2O2}\left(\frac{g_{PH2O2}}{L}\right)$$

$$r_{Ph}\left(\frac{g_{Ph}}{L\cdot h}\right) = 61{,}635 \pm 34\,\left(\frac{L}{g_{Ph\cdot h}}\right)\cdot e^{\frac{-45{,}781\pm9{,}145\left(\frac{J}{mol}\right)}{R\cdot T}}\cdot e^{-k_{d,Ph}(h^{-1})\cdot t(h)}\cdot C_{Ph}^{2}\left(\frac{g_{Ph}}{L}\right)^{2}$$

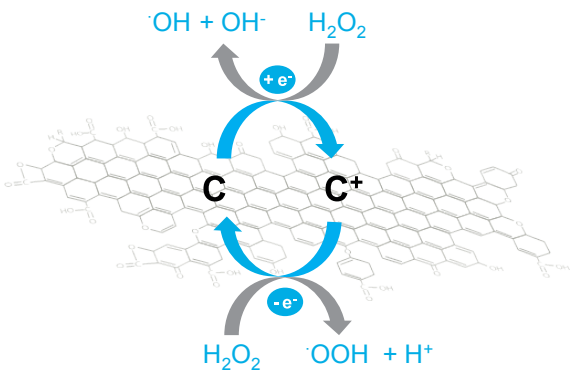
The results presented in this work, related to the use of carbon materials as catalysts for wastewater treatment of persistent organic pollutants by catalytic wet peroxide oxidation, support the following conclusions:

- The electrochemical properties of carbon materials are decisive for their catalytic activity in the hydrogen peroxide decomposition reaction. Thus, cyclic voltammetry provides a rapid, direct, and useful technique for predicting the catalytic activity of carbon materials, such as activated carbons, carbon blacks and graphites.

- The exchange current (i_o), calculated by cyclic voltametry from the representation of the applied overpotential ($E-E_{ocp}$) *vs.* the logarithm of the current intensity (I) is the overall variable governing carbon activity. The hydrogen peroxide decomposition apparent kinetic constant (k_d) is linearly dependent on it.

- The carbon content of metals, particularly iron, followed by the specific surface area and finally the content of surface oxygen groups are the mayor factors that influence the exchange current value and, therefore, the carbon catalytic activity in the hydrogen peroxide decomposition reaction.

- The limiting step in the hydrogen peroxide decomposition reaction with carbon materials is the regeneration of the active sites, which implies the oxidation of hydrogen peroxide into hydroperoxyl radicals.



- The catalytic activity of carbon materials in CWPO is determined by the efficiency of hydrogen peroxide consumption during the oxidation process. In order to have efficient catalysts, the oxidation reaction needs to be carried out under the adequate operating conditions for each specific wastewater and catalyst.

- Activated carbons and, in general, carbon materials with high specific surface area, are efficient catalysts in CWPO. High oxidation and mineralization degrees are obtained as long as organic compounds with high affinity towards activated carbon, such as phenol, are used under both high pollutant concentrations and high pollutant/carbon mass ratios (C_{phenol}=5 g/L, phenol/carbon≈2.5, 80 °C).

- Activated carbons and, in general, carbon materials with high specific surface area, are progressively deactivated during the CWPO of phenol due to the presence of condensation by-products adsorbed on their surface. Their activity can be completely restored by a thermal treatment at 350 °C in air atmosphere.

- Carbon blacks, namely carbon materials with moderate specific surface area and absence of metal impurities, such as CB-Chemviron (ref.: 2156090), are active and efficient catalysts in CWPO processes (X_{phenol}=100%, X_{TOC}=70%, η_{H2O2}=100%, 90 °C, 24 h). Interestingly, they are highly stable catalysts because their low adsorption capacity avoids the formation of adsorbed oligomeric by-products on the carbon surface, preventing its deactivation upon use.

- Graphites with significant iron content, though absolutely no-porosity such as G-Sigma-Aldrich (ref.: 282863), are active and efficient catalysts in CWPO of phenol due to the catalytic activity exhibited by the iron ashes (0.44%). The stability and reusability of this catalyst are governed by the Fe leaching resistance, depending, in last term, on the nature of the wastewater. According to this, the use of G-Sigma-Aldrich is not recommended for the treatment of wastewater containing persistent pollutants such as phenol and derivatives, whose oxidation give rise to important amounts of oxalic acid as intermediate. On the contrast, they are recommended for the treatment of winery wastewaters.

- The treatment of winery wastewaters (COD≈35 g/L, COT≈11 g/L, pH=3.8) by CWPO in the presence of a Fe-bearing graphite has proved to be an effective solution capable of dealing with the seasonal fluctuations of flow rate and

organic matter concentration. This treatment leads to rapid polyphenols depletion, generating non-toxic effluents. High oxidation and mineralization degrees are achieved ($X_{COD,TOC}$≈80%, 4 h at 125 °C, 10 atm, 5 g/L catalyst, original pH of the wastewater and the stoichiometric amount of hydrogen peroxide distributed in stepwise additions).

The results obtained in this work open the door to the employ of other type of carbon materials *viz.* graphene, graphene oxide, diamond, etc. that, with adequate electrochemical properties and under specific operating conditions that ensure efficient consumptions of hydrogen peroxide, can exhibit interesting catalytic activity in the oxidation of persistent pollutants of industrial effluents.

7

Apéndices

Apéndice I

Valores de referencia de los parámetros de contaminación

Grupo A: sustancias peligrosas

Grupo A	Vr (mg/L)
1,1,1-Tricloroetano	0,1
1,2 dicloroetano	0,01
Alacloro	0,0003
Aldrín	0,00001
Antraceno	0,0001
Arsénico	0,05
Atrazina	0,001
Benceno	0,03
Benzopireno	0,00005
Benzofluoranteno	0,00003
Benzoperileno	0,000002
Benzofluoroanteno	0,00003
C_{10-13}-cloroalcanos	0,0004
Cadmio	0,005
Cianuros totales	0,04

Grupo A	Vr (mg/L)
Clorobenceno	0,02
Clorofenvinfos	0,0001
Cloropirifos	0,00003
Cobre	0,005
Cromo	0,05
Di(2-etilhexil)ftalato	0,0013
Diclorobenceno[7]	0,02
DDT y metabolitos[8]	0,000025
Diclorometano	0,02
Dieldrín	0,00001
Pentabromodifenil éter	0,0000005
Diurón	0,0002
Endosulfán	0,000005
Endrín	0,000005
Etilbenceno	0,03
Fluoranteno	0,01
Fluoruros	1,7
Hexaclorobenceno	0,00003
Hexaclorobutaideno	0,0001
Hexaclorociclohexano	0,0001
Indeno(1,2,3-cd)pireno	0,000002
Isodrín	0,000005
Isoproturón	0,0003
Lindano	0,001
Mercurio	0,001
Metolacloro	0,001

Grupo A	Vr (mg/L)
Naftaleno	0,005
Níquel	0,05
Nonifenoles	0,0003
Octifenoles	0,0001
Pentaclorobenceno	0,000007
Pentaclorofenol	0,002
Percloroetileno	0,01
Plomo	0,05
Selenio	0,001
Simazina	0,001
Terbutilazina	0,001
Tetracloruro de Carbono	0,012
Tolueno	0,05
Tributilestaño	0,00002
Triclrobencenos	0,0004
Tricloroetileno	0,01
Cloroformo	0,012
Trifluralina	0,00003
Xileno[9]	0,03
Zinc total	0,03

Vr: valor límite de referencia

[7] *Suma de los isómeros orto, meta y para diclorobenceno.*

[8] *Suma de los isómeros p,p´-DDT + o,p´-DDT + p,p´-DDE + p,p´-DDD.*

[9] *Suma de los isómeros orto-, meta- y para-xileno.*

Grupo B: contaminantes

Grupo B	Vr (mg/L)
Amonio total	1
Bario	1
Berilio	1
Boro	1
Cloro total	0,005
Cobalto	1
Indice de fenoles	0,1
Fósforo total	0.4
Fosfatos	0,7
Hidrocarburos método IR	1
Hierro	2
Manganeso	1
Magnesio	1
Nitratos	50
Nitritos	0,03
Nitrógeno Kjeldahl	3
Nitrógeno total	3
Tensoactivos aniónicos	0,5
Toxicidad en UT	1
Vanadio	1
Biocidas y productos fitosanitarios	0,001

Vr: valor límite de referencia

Grupo C: otros contaminantes

Grupo C	Unidades	Vr
Incremento de temperatura del agua	ºC	Incremento= 3ºC
ph	Unidades de pH	5,5-9
Conductividad eléctrica a 20ºC	µS/cm	1000
Cloruros	mg/L	200
Sulfatos	mg/L	250
Color	mg Pt/L	200
Sólidos en suspensión	mg/L	25
Demanda bioquímica de oxígeno (DBO_5 a 20ºC) sin nitrificación	mg/L	7
Demanda química de oxígeno	mg/L	30
Coliformes fecales	UFC/100 mL	20000
Coliformes totales 37 ºC	UFC/100 mL	50000
Enterovirus	PFU/10 mL	0
Estreptococos fecales	UFC/100 mL	10000
Salmonelas	En 1L	Ausencia
Otros parámetros microbiológicos		

Vr: valor límite de referencia

Apéndice II:

Nomenclatura

AE	Análisis elemental
A_{ext}	Area externa
AOP	Procesos de oxidación avanzada
b	Pendiente de tafel
BE	Energía de enlace
C_i	Concentración
C	Estado reducido de un material carbonoso
C^+	Estado oxidado de un material carbonoso
CC	Carga culómbica
COT	Carbono orgánico total
CV	ciclyc voltammetry
CWAO	Oxidación húmeda catalítica con aire
CWPO	Oxidación húmeda catalítica con peróxido de hidrógeno
d_{002}	Valor del espacio entre capas
D_{eff}	Coeficiente de difusión en carbones activados

d_p	Diámetro de partícula
DQO	Demanda química de oxígeno
DRIFTS	Espectroscopía de transformada de Furier y reflectancia difusa infraroja
DTG	Análisis termogravimétrico diferencial
E	Potential
Ea	Energía de activación
EDAR	Estación depuradora de aguas residuales
EDI	Electrodesionización
EDR	Electrodiálisis reversa
E_{ocp}	Potencial en circuito abierto
E_{onset}	Potencial *onset*
FTIR	Espectroscopía infrarroja de transformada de Furier
G	Grafito
GC	Cromatografía de gas
GSO	Grupos superficiales oxigenados
H_2O_2	Peróxido de hidrógeno
H_2O_2-CWAO	Oxidación húmeda catalítica con aire promovida por H_2O_2
H_2O_2-WAO	Oxidación húmeda con aire promovida por H_2O_2
HAP	Hidroxiapatita
HPLC	Cromatografía de líquidos de alta resolución
I	Intensidad de corriente

IC	Cromatrografía iónica
IC_{50}	Porcentaje de dilución de la muestra que reduce en un 50% la luz emitida por los microorganismos
ICP	Plasma de acoplamiento inductivo
i_o	Corriente de intercambio del proceso
K_{app}	Constante cinética aparente
K_d	Constante cinética aparente
$K_{d,i}$	Constante cinética de desactivación
$K_{cat,}$ $K_{d,cat}$	Constante cinética del catalizador
K_{Ph}	Constante cinética de la oxidación de fenol
$K_{Ph'}$	Constante cinética modificada de la oxidación de fenol
k_{H2O2}	Constante cinética de la descomposición de peróxido de hidrógeno
L_a	Diámetro medio cristalino
L_c	Altura media cristalina
L_s	Longitud característica de la partícula de catalizador
M	Molaridad
MBR	Reactor biológico de membrana
MF	Microfiltración
MOF	Plantillas metal-orgánica
NF	Nanofiltración
NH	Negro de humo
OI	Ósmosis inversa

P	Presión
R	Constante de los gases ideales
RBC	Reactor biológico rotativo
r	Velocidad de reacción
r_o	Velocidad inicial de reacción
reg-AC	Carbon activado regenerado
r_{obs}	Velocidad de reacción volumétrica observada
rpm	Revolución por minuto
S_{BET}	Área específica BET
SBR	Reactor secuencial de flujo discontinuo
SCWO	Oxidación húmeda supercrítica
SPME	Microextracción en fase sólida
t	Tiempo
T	Temperatura
TEM	Microscopía de transmisión electrónica
TGA	Análisis termogravimétrico
TPD	Desorción térmica programada
TPO	Oxidación térmica programada
TU	Unidades de toxicidad
TXRF	Fluorescencia de rayos X por reflexión total
UF	Ultrafiltración

UV	Ultravioleta
v	Velocidad de barrido
VC	Voltametría cíclica
V_m	Volumen de microporos
w-AC	Carbón activado prelavado con una disolución de fenol
WAO	Oxidación húmeda con aire
WPO	Oxidación húmeda con peróxido de hidrógeno
X	Conversión
XPS	Espectroscopía fotoelectrónica de rayos X
XRD	Difracción de rayos X
ϕ	Módulo de Thiele
η_{H2O2}	Eficiencia en el consume de peróxido de hidrógeno
η	Factor de efectividad del catalizador
φ	Módulo de Wheeler-Weisz

Nomenclature

AC	Activated carbon
A_{ext}	External area or non-microporous surface area
AOP	Advance oxidation process
b	Tafel slope
BE	Binding energies
C_i	Concentration
C	Reduced carbon state
C^+	Oxidized carbon state
CB	Carbon black
CC	Coulombic charge
COD	Chemical oxygen demand
CV	Ciclyc voltammetry
CWAO	Catalytic wet air oxidation
CWPO	Catalytic wet peroxide oxidation
d_{002}	Interlayer spacing value
D_{eff}	Effective diffusivity in activated carbon
dp	Diameter of the particles
DRIFTS	Diffuse reflectance infrared Fourier transform spectroscopy

DTG	Derivative thermogravimetric analysis
E	Potential
Ea	activation energy
EA	Elemental analysis
E_{ocp}	Open circuit potential
E_{onset}	Onset potential
FTIR	Fourier transform infrared spectroscopy
G	Graphite
GC	Gas chromatography
H_2O_2	Hydrogen peroxide
H_2O_2-CWAO	Hydrogen peroxide promoted catalytic wet air oxidation
H_2O_2-WAO	Hydrogen peroxide promoted wet air oxidation
HAP	Hydroxyapatite
HPLC	High performance liquid chromatography
I	Current intensity
IC	Ionic chromatography
IC_{50}	sample dilution percentage that yields 50% reduction of the light emitted by the microorganisms.
ICP	Induced coupled plasma
i_o	Current exchange
K_{app}	Apparent kinetic constant
K_d	Apparent kinetic constant

$K_{d,i}$	Deactivation kinetic constant
$K_{cat,}$ $K_{d,cat}$	Catalyst kinetic rate constant
K_{Ph}	Kinetic rate constant for phenol oxidation
$K_{Ph'}$	Modified kinetic rate constant for phenol oxidation
k_{H2O2}	Kinetic rate constant for hydrogen peroxide decomposition
L_a	Average crystalline diameter
L_c	Average crystalline height
L_s	Characteristic length of the catalyst particle
M	Molarity
MOF	Metal organic framework
P	Pressure
Ph	Phenol
R	Gas constant
r	Reaction rate
r_o	Initial reaction rate
reg-AC	Regenerated activated carbon
r_{obs}	Observed volumetric reaction rate
rpm	Revolution per minute
SAR	Sodicity
S_{BET}	BET surface area
SCWO	Supercritical wet oxidation

SOG	Surface oxygen groups
SPME	Solid-phase microextraction
SUWOX	Supercritical water oxidation
t	Time
T	Temperature
TEM	Transmission electron microscope
TGA	Thermal gravimetric analysis
TON	Turnover number
TOF	Turnover frecuency
TOC	Total organic carbon
TPD	Temperature programmed desorption
TPO	Temperature programmed oxidation
TU	Toxicity unit
TXRF	Total reflection X-ray fluorescence
UV	Ultraviolet
V	Sweep rate
V_m	micropore volume
w	Weight
w-AC	Phenol pre-washed activated carbons
WAO	Water air oxidation
WPO	Wet peroxide oxidation

X	Conversion
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ϕ	Thiele modulus
η_{H2O2}	Efficiency of hydrogen peroxide consumption
η	Catalyst effectiveness factor
φ	Wheeler-Weisz modulus

Apéndice III

Otras publicaciones

Artículos:

Degradation of Ionic Liquids by Fenton Oxidation. M. Munoz, ***C. M. Domínguez***, Z.M. de Pedro, A. Quintanilla, J.A. Casas, J.J. Rodriguez. Submitted to Catalysis Today. Special issue EAAOP3 Congress.

Imidazolium-based ionic liquids breakdown by Fenton oxidation: ecotoxicity study. ***C. M. Domínguez***, M. Munoz, A. Quintanilla, Z.M. de Pedro, S.P.M. Ventura, J.A.P. Coutinho, J.A. Casas, J.J. Rodriguez. Submitted to Journal of Chemical Technology and Biotechnology. Special issue EAAOP3 Congress.

Catalizadores de carbón para procesos de oxidación húmeda con peróxido de hidrogeno. A. Quintanilla, A. Rey, ***C. M. Domínguez***, N. Alonso-Morales, M.A. Gilarranz, J.A. Casas, J.J. Rodriguez, Ingeniería Química (2011) 500, 120-124.

Capítulos de libro:

Emerging Catalysts for Wet Air Oxidation Process. A. Quintanilla, ***C. M. Domínguez***, J.A. Casas, J.J. In: Minjae Ghang and Bjorn Ramel (Ed.), Focus on Catalysis Reserach: New Developments, Nova Science Publishers, Inc., 237-260.

Imidazolium-based ionic liquids breakdown by Fenton oxidation: ecotoxicity study

P183

C.M. Domínguez[1], *M. Munoz*[1], *A. Quintanilla*[1], *Z.M. de Pedro*[1], *S.P.M. Ventura*[2], *J.A.P. Coutinho*[2], *J.A. Casas*[1], *J.J. Rodriguez*[1]

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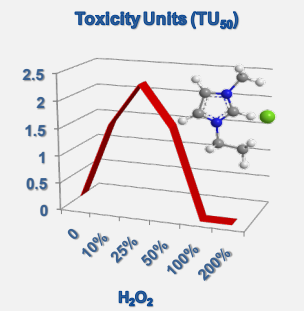

This study explores the effect of the structural variations of the ionic liquids (ILs), *viz.* alkyl chain length and anion type, on the ecotoxicity of the effluents obtained from the Fenton process. The imidazolium ionic liquid (IL) family has been selected as a target family. The oxidation was carried out batch-wise at the following initial conditions $[IL]_0$=1000 mg·L^{-1}, $[Fe]_0$=50 mg·L^{-1}, $[H_2O_2]_0$=10-200% stoichiometric dose for complete IL removal, T=70 ºC, pH_0=3 and t≤4 h. At these operating conditions the ecotoxicity of the Fenton effluents was negligible as long as the 70% of TOC removal was achieved. Therefore, Fenton oxidation must be carried out using stocihiometric amount of H_2O_2 from comlpete ILs oxidation. The effect of the alkyl chain length on ecotoxicity of the final effluents was negligible while the anion type, in particular the organic anions, needs to be cautiously considered.

1. Introduction

In the last years, ionic liquids (ILs) have gained considerable attention as organic solvents for a broad range of industrial applications [1]. Their wide applicability could soon result in their production and use on an industrial scale. Therefore, certain amounts of ILs will be present in industrial wastewaters as persistent pollutants [2]. The toxicity and biodegradability of these compounds need to be measured in order to select the appropriate technology for its removal. Advanced oxidation processes are efficient alternatives to remove harmful organic pollutants in wastewater by oxidation with hydroxyl and hydroperoxy radicals produced by different ways [3]. Among them, the Fenton process (Fe/H_2O_2) has been applied to wastewater containing imidazolium and pyridinium-based ILs [4, 5]. The complete IL removal is obtained in 150 min of reaction time. In these studies, scarce attention has been paid on the intermediates and by-products of the oxidation, and neither the progress of total organic carbon nor the ecotoxicity of the Fenton effluents have been measured. Moreover, H_2O_2 doses above the stoichiometric one has been used.

The present work studies the effect of the structural variations of the ILs, such as the alkyl chain length and anion type, on the ecotoxicity of the effluents obtained from the Fenton process. It is known that modifications of these issues lead to important changes in chemical and physical properties of ILs [6]. The dose of H_2O_2, the main aspect to assess the cost-effectiveness of Fenton process has been also studied. In this study, several imidazolium-based ILs have been selected as a IL representative family.

2. Experimental

The ILs used in this study were supplied by different companies such as Sigma-Aldrich, Solchemar and Iolitec, always with purity over 98 wt%. The hydrogen peroxide solution (30 wt%) and $Fe(NO_3)_3$ salt were purchased at Sigma-Aldrich and Panreac, respectively.

The oxidation tests were carried out batch-wise in a glass reactor shaken in a constant-temperature bath at an equivalent stirring velocity of 200 rpm. The IL solution (48 mL, 1000 mg·L^{-1}) at pH=3 (HNO_3) was placed in the reactor and heated to 70 ºC. When temperature was equilibrated, 1 mL of the hydrogen peroxide solution (at the appropiate concentration to obtain the desired H_2O_2/IL molar ratio) and 1 mL of the $Fe(NO_3)_3$ aqueous solution (C_{Fe}=50 mg/L), were injected. After 4 h of reaction, the heating was switched-off, the reactor was cooled to room temperature and the effluents were then analyzed. The ILs were identified and quantified by high performance liquid chromatography with a mass spectrometer (HPLC-MS, Agilent 6120). Total organic carbon (TOC) was measured in a Shimadzu TOC VSCH analyzer. The absence of H_2O_2 in the effluents was confirmed with a colorimetric method [7]. The ecotoxicity of the samples was measured by a standard toxicity test conducted with the luminescent bacteria *Vibrio fischeri* (Microtox®; Azur Environmental 1998). This bioassay is based on the decrease of the light emission by the bacterium as the result of its exposure to a toxicant at 15 ºC for 15 min. The IC_{50} (dilution ratio of the sample that produces 50% of light emission inhibition) values were estimated through the Microtox® Omni™ Software version 4.3.0.1(Microtox®; Azur Environmental 1998 [8]).

3. Results and discussion

3.1. Effect of the H_2O_2 dose on [C_2mim][Cl] Fenton oxidation.

Figure 1 shows the results obtained in the Fenton oxidation of [C_2mim][Cl] at different initial H_2O_2 concentrations ranged from 0 to 200% of the the theoretical stoichiometric amount to the complete IL oxidation. The IL disappearence and TOC removal gradually increase with the amount of H_2O_2 up to reach the asymptotic value at complete IL conversion and 70% of TOC depletion. Thereby, the existence of refractory by-products is evident at the used operating conditions.

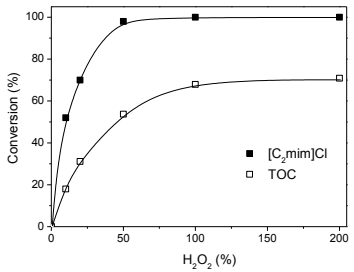

Figure 1. Influence of the H_2O_2 dose in [C_2mim][Cl] and TOC conversions. $[IL]_0$=1000 mg·L^{-1}, $[Fe]_0$=50 mg·L^{-1}, T=70 ºC, pH_0=3, t≤4h.

Table 1 summarizes the ecotoxicity values for the [C_2mim]Cl starting solution and for the final effluents obtained in the Fenton oxidation of this IL at different initial H_2O_2 concentrations. As can be observed, at least the stoichiometric amount of H_2O_2 must be used in oder to obtain non-ecotoxic Fenton effluents. Therefore, the ecotoxicity of the by-products obtained at TOC removals of 70% achieved at these H_2O_2 doses (Figure 1) is negligible.

Table 1. Ecotoxicity data ($IC_{50,}$ mg·L^{-1}) for [C_2mim][Cl] initial solution and its Fenton effluents at different initial H_2O_2 doses. $[IL]_0$=1000 mg·L^{-1}, $[Fe]_0$=50 mg·L^{-1}, T=70 ºC, pH_0=3, t≤4h.

H_2O_2 dose	IL	effluent
10%		62.6
20%		42.6
50%	474.7	61.7
100%		n.t.[a]
200%		n.t.[a]

[a]non-toxic.

The use of sub-stoichiometric H_2O_2 doses is inadvisable since not only a less mineralization is reached but also ecotoxic effluents are yielded, which is in agreement with the results obtained in the Fenton oxidation of chlorophenols [9]. Therefore, the mineralization of the IL along with its oxidation must be measured when assessing suitability of advanced oxidation treatments.

3.2. Effect of the alkyl chain length

Figure 2 illustrates the IL and TOC conversions obtained once hydrogen peroxide is totally consumed for imidazolium chloride-based ILs with a chain length ranged from C_2 to C_{16}. As can be seen, there is no influence of the chain lenght on the Fenton performance at the selected operation conditions. In all cases, the complete IL conversion and around 70% TOC removal were achieved upon 4 h of reaction.

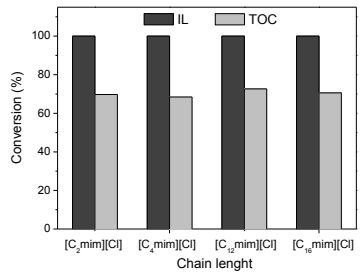

Figure 2. Influence of the alkyl chain length on the IL and TOC conversions. $[IL]_0$=1000 mg·L^{-1}, $[Fe]_0$=50mg·L^{-1}, $[H_2O_2]_0$=stoichiometric dose, T=70 ºC, pH_0=3, t≤4h.

The ecotoxicity values of the initial ILs solutions and the final effluents of Figure 2, collected in Table 2, indicates that the increase of the alkyl chain length leads to a pronounced increase in the ecotoxicity (IC_{50} values from 474.7 to 0.03 mg·L^{-1} for C_2 and C_{16}, respectively), which is consistent with previous studies [10, 11]. Interestingly, the Fenton effluents were considered as non-toxic in all cases of [$C_{2\text{-}16}$mim][Cl].

Table 2. Ecotoxicity data ($IC_{50,}$ mg·L^{-1}) of ILs and the Fenton effluents. $[IL]_0$=1000 mg·L^{-1}, $[Fe]_0$=50 mg·L^{-1}, $[H_2O_2]_0$=stoichiometric dose, T=70 ºC, pH_0=3, t≤4h.

Cation	Anion	IL	effluent
$[C_2mim]^+$	$[Cl]^-$	474.7	n.t [a]
$[C_4mim]^+$		62.4	n.t [a]
$[C_{12}mim]^+$		0.10	583.3
$[C_{16}mim]^+$		0.03	492.8

[a]non-toxic.

3.2.Effect of the anion type

Figure 3 shows the oxidation results obtained in the treatment of several 1-butyl-3-methylimidazolium salts ($[C_4mim]^+$) conjugated with different anions, *viz.* chloride ($[Cl]^-$), methanesulfonate ($[CH_3SO_3]^-$), methylsulfate ($[CH_3SO_4]^-$) and acetate ($[CH_3CO_2]^-$).

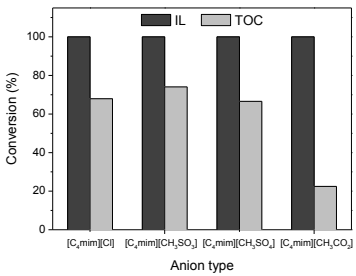

Figure 3. Influence of the anion type on the IL and TOC conversions. $[IL]_0$=1000mg·L^{-1}, $[Fe]_0$=50 mg·L^{-1} $[H_2O_2]_0$=stoichiometric dose, T=70 ºC, pH_0=3, t≤4h.

As can be observed, the total depletion of ILs was always achieved. However, the TOC removal was affected by the anion nature. In the case of acetate, TOC was significantly lower in comparison with the values of inorganic anions. This can be associated to the fact that, in the presence of methylimidazolium acetate, iron precipitated upon reaction.

The results obtained in the ecotoxicity analyses of the initial ILs solutions as well as the different effluents of Figure 3 are given in Table 3. As it is shown, the anion effect is not relevant on the ecotoxicity of the initial IL solutions, independently of the anion conjugated ($[Cl]^-$, $[CH_3SO_3]^-$, $[CH_3SO_4]^-$, and $[CH_3CO_2]^-$). However, important differences in terms of ecotoxicity can be found in the Fenton effluents. While null or very low ecotoxicity values are reached for $[Cl]^-$, $[CH_3SO_3]^-$ and $[CH_3SO_4]^-$ anions, in the case of $[CH_3CO_2]^-$ anion, the effluent is more toxic than the starting IL. This result indicates that the Fenton treatment must provide high mineralization degrees, at least, higher than those obtained at 70 ºC with $[C_4mim][CH_3CO_2]$ (X_{TOC}≈25%, Figure 3) in order to avoid oxidation by-products with similar or even higher toxicity values than the initial IL.

Table 3. Ecotoxicity data ($IC_{50,}$ mg·L^{-1}) of ILs and the Fenton effluents. $[IL]_0$=1000 mg·L^{-1}, $[Fe]_0$=50 mg·L^{-1}, $[H_2O_2]_0$=stoichiometric dose, T=70 ºC, pH_0=3, t≤4h.

Cation	Anion	IL	effluent
$[C_4mim]^+$	$[Cl]^-$	62.4	n.t.[a]
	$[CH_3SO_3]^-$	122.5	n.t.[a]
	$[CH_3SO_4]^-$	106.4	716.6
	$[CH_3CO_2]^-$	61.5	49.2

[a]non-toxic.

4. Conclusions

Fenton oxidation represents an interesting option for the ILs degradation. Total oxidation of ILs and 70% TOC removal were achieved upon Fenton with $[IL]_0$=1000 mg·L^{-1}, $[H_2O_2]_0$=stoichiometric dose, $[Fe]_0$=50 mg·L^{-1}, T=70 ºC and pH_0=3 as initial conditions. Only the anion type has a significant influence on the TOC removal, particularly when the $[C_2mim][CH_3CO_2]$ is used, where a mineralization degree significantly lower than those obtained with inorganic anions was achieved.

The ecotoxicity of the Fenton effluents was negligible as long as the 70% of TOC removal was achieved. Then, in the $[C_2mim][CH_3CO_2]$ case, and when sub-stoichiometric amounts of H_2O_2 are employed, the toxicity of the treated ILs was higher than the starting ones. Thus, the possibility of reducing H_2O_2 consumption is limited dealing with ILs oxidation.

Acknowledgements

The authors are gratful to the Spanish MICINN for the financial support through the projects CTQ2008-03988/PPQ, CTQ2010-14807 and S2009/AMB-1588. The authors are grateful for financial support from FEDER funds through the program COMPETE and by national fund through the Portuguese Foundation for Science and Technology (FCT) under the scope of the projects Pest-C/CTM/LA0011/2011 and PTDC/AAC-AMB/119172/2010. The authors also thank financial support through the post-doctoral grants SFRH/BPD/79263/2011of S.P.M.Ventura.

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Degradation of Ionic Liquids by Fenton Oxidation

P191

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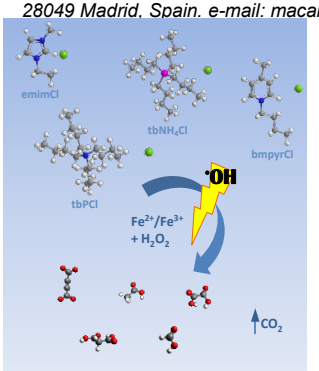

Fenton oxidation has proved to be a highly efficient treatment for the removal of several ionic liquids families *viz.* imdazolium, pyridinium, ammonium and phosphonium. Both aromatics (imdazolium and pyridinium) and aliphatics (ammonium and phosphonium) were effectively degraded, though significant differences were obtained among them. The operating condition study showed that the use of temperatures above the ambient permits a significant decrease in the Fe and hydrogen peroxide doses without negative effects on the efficiency of the treament. Thereby, 50 mg·L^{-1} Fe^{3+} and the stoichiometric amount of H_2O_2 for complete IL oxidation can be used at 70-90 ºC. Under these conditions, complete oxidation of ILs and non-ecotoxic effluents, mainly consisted on low weight organic acids, were obtained at 4 h reaction time.

1. Introduction

Ionic liquids (ILs) are attracting attention due to their particular properties, such as extremely low vapor pressure, high thermal and chemical stabilities, non-flammability and high solvent capacity [1,2]. They have been termed “designer solvents” since their polarity and hydrophilicity/hydrophobicity can be tuned by a suitable combination of cation and anion [3]. In this sense, the number of commercial applications of ILs is increasing noticeably and the rate of appearance of patents on IL technology has been rising exponentially in the last years.

Although ILs show a very low vapor pressure reducing the environmental risks for air pollution, water solubilities of many ILs are not negligible, and the release of them into aquatic environments may lead to water pollution and related risks [4]. Since ILs applications in industry commonly involve water streams and synthesis routes frequently include aqueous media, it can be expected that certain amounts of ILs will soon be present in industrial wastewater. This represents a major environmental concern since ILs present a high stability and could stay in aquatic ecosystems as persistent pollutants. Moreover, they usually present a high toxicity to various life forms at different levels of biological complexity [4,5]. In this context, the development of effective methods for the degradation of these potential pollutants, either to less harmful intermediates or to complete mineralization is demanding increasing attention.

Advanced oxidation processes, based on the action of hydroxyl radicals at near ambient temperature and pressure, can be regarded as a potential solution for ILs removal. Among these oxidation techniques, the Fenton process using H_2O_2 and iron salts is one of the most effective. It is based on the catalytic decomposition of H_2O_2 by means of iron at acid pH, giving rise to hydroxyl radicals. Fenton process has been successfully applied in the treatment of a wide range of organic pollutants as well as industrial wastewater [6,7]. So far, only few works have been reported dealing with the degradation of ILs by Fenton oxidation [8,9]. Those studies have been focused on the destruction of the ILs (imidazolium and pyridinium families) using large amounts of H_2O_2 and not providing information about TOC reduction and effluents ecotoxicity. Nevertheless, the extended implementation of this technology requires better knowledge of its performance at lower levels of H_2O_2 consumption to assure the cost-effectiveness of the process.

The aim of this work is to study the suitability of the Fenton process for the degradation of four families of ILs, including aromatic and non-aromatic cations using the stoichiometric H_2O_2 dose. Experiments were performed addressing the effect of catalyst concentration as well as temperature on ILs conversion and mineralization. The ecotoxicity of the oxidation effluents was also determined by the Microtox® test.

2. Materials and methods

Oxidation runs at 4 h reaction time were carried out in 100 mL glass batch reactors shaken in a constant-temperature bath at an equivalent stirring velocity around 200 rpm. The initial pH value was adjusted to 3 with nitric acid. The ILs used were: 1-ethyl-3-methylimidazolium chloride (emimCl), 1-butyl-4-methylpyridinium chloride (bmpyrCl), tetrabutylammonium chloride ($tbNH_4Cl$) and tetrabutylphosphonium chloride (tbPCl)). A 1000 mg·L^{-1} starting concentration of each IL and the theoretical stoichiometric amount of H_2O_2 for the complete oxidation of the IL organic cations were always used. The Fe^{3+} dose was varied in the range from 50 to 125 mg·L^{-1}, while the temperature effect was tested at 50-90 ºC.

The progress of the reactions was followed by periodically withdrawing and analyzing liquid samples from the reactor. ILs were quantified by HPLC-MS (Varian). Short-chain organic acids were analyzed by ion chromatography (Metrohm 790 IC). A TOC Analyzer (Shimadzu TOC-VCSH) was used to measure the total organic carbon. The H_2O_2 measurement was performed by a colorimetric method. The ecotoxicity of both target pollutants and oxidation effluents was determined by means of a bioassay following the standard Microtox procedure.

3. Results and discussion

3.1. Operating conditions study

The effect of Fe dose as well as temperature on the conversion of TOC and H_2O_2 upon emimCl Fenton oxidation at 60 min reaction time is depicted in Figure 1. As observed, the increase of temperature improved the conversion of both TOC and H_2O_2. This effect was more pronounced when using low Fe concentrations (50 mg·L^{-1}) which led to the same TOC reduction as the highest Fe dose (125 mg·L^{-1}) working at temperatures above 70 ºC. This fact is particularly important since the use of low iron doses would reduce the amount of $Fe(OH)_3$ sludge produced upon the effluent neutralization step. According to these results, increasing the temperature is a better strategy than stressing the Fe dose.

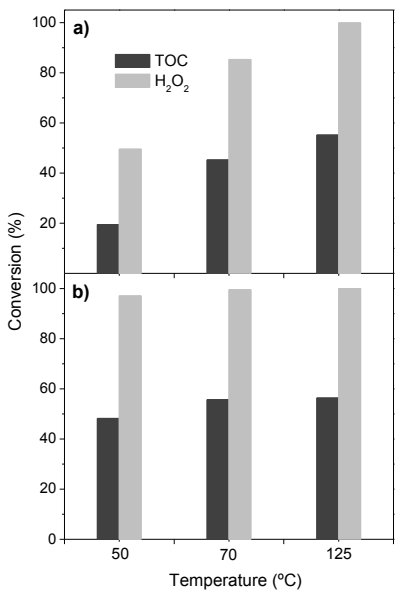

Figure 1. Effect of Fe dose (a: 50 mg·L^{-1}; b: 125 mg·L^{-1}) on TOC and H_2O_2 conversion upon Fenton oxidation of emimCl at different temperatures. ([emimCl]$_0$ = 1000 mg·L^{-1}; [H_2O_2]$_0$ = 4000 mg·L^{-1}; pH$_0$ = 3; t = 60min).

Figure 2 shows the evolution of emimCl, TOC and H_2O_2 conversions upon Fenton oxidation at different temperatures. As observed, a dramatic improvement of emimCl removal as well as TOC reduction and H_2O_2 decomposition was achieved as temperature increased, especially from 50 ºC to 70 ºC. Moreover, the efficiency on the use of H_2O_2 (X_{TOC}/X_{H2O2}) was improved from 43% at 50 ºC to 53% at 70ºC, not obtaining much better efficiencies working at 90 ºC (56%). Therefore, the selected operating temperature for further experiments dealing with ILs was 70 ºC. These results are in good agreement with those obtained by Zazo et al. [10], who demonstrated that higher temperatures lead to a more efficient use of H_2O_2 upon enhanced generation of ·OH radicals at low Fe concentration.

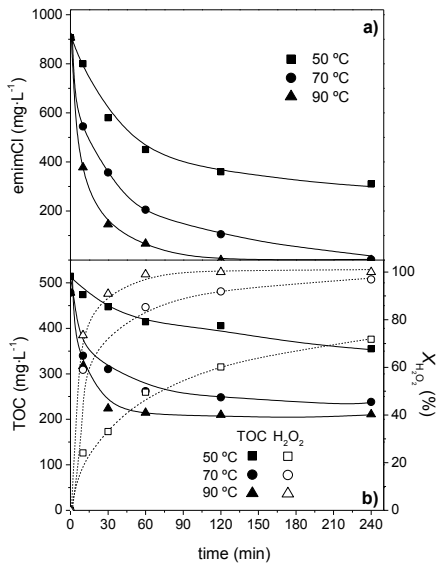

Figure 2. Influence of temperature on emimCl evolution (a) and TOC reduction and H_2O_2 conversion (b). ([emimCl]$_0$ = 1000 mg·L^{-1}; [H_2O_2]$_0$ = 4000 mg·L^{-1}; [Fe^{3+}]$_0$ = 50 mg·L^{-1}; pH$_0$ = 3).

3.2. Fenton oxidation of four ILs families

Once selected the operating conditions (50 mg·L^{-1} Fe^{3+}, 70 ºC), the oxidation of four ILs families, imdazolium, pyridinium, ammonium and phosphonium, was studied. Table 1 summarizes the conversion values of TOC and H_2O_2 after 4h Fenton oxidation at 70 ºC as well as the apparent kinetic constant values obtained under these operating conditions. The complete removal of the four ILs tested was achieved but important differences were obtained regarding the TOC reduction as well as H_2O_2 decomposition. As seen, imdazolium type is significantly more degradable than the others, which can be explained based on the nature of the IL. The aromatic ILs, with

delocalized electrons, are faster mineralized than those with aliphatic character. Among the later, differences were also obtained because phosphonium was less mineralized than pyridinium and ammonium families. This is consisting with the resulting decomposition rate of H_2O_2. The reason could be associated to a decrease in iron activity, because iron (III) can be forming complexes with organic intermediates, thus its regeneration is impeded. In this sense, further studies are now in progress.

Table 1. TOC and H_2O_2 conversion and apparent kinetic constants values from Fenton oxidation of four ILs families. ($[IL]_0$ = 1000 mg·L^{-1}; $[H_2O_2]_0$ = stoichiometric dose; $[Fe^{3+}]_0$ = 50 mg·L^{-1}; T = 70 ºC; pH_0 = 3).

Ionic liquid	TOC		H_2O_2	
	X **(%)**	**k** (L·mg-1·min^{-1})	***X*** **(%)**	**k** (min^{-1})
emimCl	55.3	38.5	96.7	16.4
bmpyrCl	35.7	5.2	97.9	15.3
tbNH$_4$Cl	38.2	7.1	98.9	21.8
tbPCl	28.2	4.1	76.6	8.7

3.3. Ecotoxicity study

The ecotoxicity of the effluents at 4 h reaction time was measured along with the initial ILs solutions. As can be seen in Table 2, increasing the reaction temperature allowed obtaining final effluents with significantly higher IC_{50} values, and thus, lower toxicity values than the starting ILs solutions. Thereby negligible ecotoxicity was observed for the final effluents when the process was performed at 90 ºC. The higher ecotoxicity of the effluents obtained at 50 ºC must be mainly due to the intermediates formed in the process since working at this temperature the mineralization degree was really low (<20% in all cases) and small amounts of short-chain organic acids were obtained.

Table 2. Ecotoxicity values (IC_{50}) after 4 h of the Fenton oxidation of ILs at different temperatures. ($[IL]_0$ = 1000 mg·L^{-1}; $[H_2O_2]_0$ = stoichiometric dose; $[Fe^{3+}]_0$ = 50 mg·L^{-1}).

Ionic liquid	Initial sample	Oxidation effluents		
		50 ºC	**70 ºC**	**90 ºC**
emimCl	474.7	25.1	n.t.[a]	n.t.[a]
bmpyrCl	29.8	7.71	590.9	n.t.[a]
tbNH$_4$Cl	46.9	22.1	n.t.[a]	n.t.[a]
tbPCl	17.2	10.1	410.3	n.t.[a]

[a] non-toxic.

4. Conclusions

Fenton oxidation at temperatures above the ambient is an efficient treatment for the removal of ILs. Complete ILs disappearance was achieved from 1000 mg·L^{-1} starting solutions at low iron (50 mg·L^{-1}) and H_2O_2 doses (stoichiometric amount for complete IL oxidation) at 70 ºC. Although further research is needed in order to determine the nature of the by-products obtained upon ILs oxidation, those compounds mainly evolve to short-chain organic acids working at temperatures above 70 ºC. Under those operating conditions, Fenton oxidation allowed a dramatic reduction of ecotoxicity.

Acknowledgements
This research has been supported by the Spanish MICINN through the projects CTQ2008-03988 and CTQ2010-14807 by the CM through the project S-2009/AMB-1588. M. Munoz thanks the Spanish Ministry of Education for a FPU research grant.

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TRATAMIENTO DE AGUAS RESIDUALES

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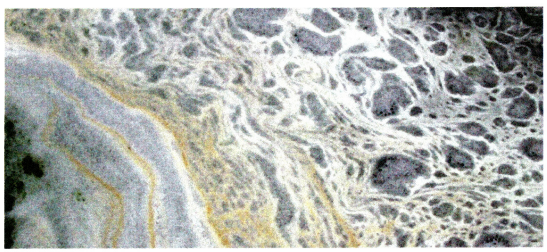


Catalizadores de carbón en procesos de oxidación húmeda con peróxido de hidrógeno

Para el tratamiento de aguas residuales industriales

Se estudia la aplicación práctica de distintos materiales carbonosos (dos carbones activados, un negro de humo y un material con estructura equivalente al negro de humo pero exento de porosidad preparado a partir de polietileno de baja densidad) como catalizadores de bajo coste en procesos de oxidación húmeda con peróxido de hidrógeno. En este trabajo se particulariza para el tratamiento de aguas fenólicas con una carga de DQO media (3.000-15.000 mg/L).

EL PROCESO DE OXIDACIÓN HÚMEDA con peróxido de hidrógeno es una tecnología con una consolidada implantación industrial en el tratamiento de aguas residuales industriales de contaminación media (cargas de DQO entre 2.000 y 20.000 mg/L). El éxito de este proceso consiste en la generación, en condiciones económicas aceptables, de especies con un alto potencial de oxidación, como son los radicales hidroxilo (OH). Estas especies son capaces de reaccionar con una amplia gama de compuestos orgánicos de forma poco selectiva [1] y se producen en condiciones ambientales (presión atmosférica y temperatura ambiental) por la descomposición del peróxido de hidrógeno en presencia de un reductor (muy comúnmente, alguna sal de hierro divalente disuelta), de acuerdo con las siguientes reacciones:

1 $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^-$

2 $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\cdot}OOH + H^+$

La Figura 1 muestra el esquema simplificado para este tipo de procesos, que en el caso particular del sistema Fe^{2+}/H_2O_2 recibe el nombre de proceso Fenton.

La creciente actividad industrial, así como el establecimiento de una legislación ambiental cada vez más severa [2], han justificado la intensificación de esta tecnología mediante el endurecimiento de las condiciones de operación. Así, en la actualidad se emplean presiones en torno a 2-5 atm y temperaturas de hasta 130 ºC, y aún en estas condiciones, la oxidación húmeda con peróxido de hidrógeno, empleando como catalizador una sal de hierro disuelta, es un proceso competitivo, como muestran las unidades comerciales de US Peroxide, OXY-PURE®, OHP® y PROX T.E.C [3].

El proceso Fenton resulta una solución atractiva por la simplicidad de diseño y la sencillez de operación, debido, por un lado, a la abundancia y bajo coste del hierro y, por otro, a la facilidad de manejo del peróxido de hidrógeno y su descomposición a productos inocuos para el medio ambiente. No obstante, el proceso Fenton también presenta inconvenientes, como son el precio del peróxido de hidrógeno, elevado en comparación con otros oxidantes, y la dependencia de la actividad catalítica con el pH del agua a tratar. El sistema Fe^{2+}/H_2O_2 presenta la máxima actividad a un pH alrededor de 3, lo que ha de tenerse en cuenta en la selección de los materiales, y obliga a la incorporación de una etapa de ajuste de pH del agua a tratar y la consiguiente neutralización del efluente final (Figura 1).

Un inconveniente importante deriva de la pérdida continua del catalizador (añadido como Fe2+) en el efluente, que, además, implica la necesidad de separarlo del mismo y gestionar de manera adecuada los lodos de hidróxido de hierro generados en la neutralización, que pueden arrastrar materia orgánica en suspensión y/o adsorbida. Una posible solución a este problema consiste en el empleo de catalizadores sólidos, en los que el hierro se encuentre inmovilizado y adecuadamente disperso sobre un soporte. Este tipo de tratamiento se conoce como proceso Fenton heterogéneo, ya que la fase activa, generalmente hierro, no se encuentra en disolución, sino formando parte del sólido.

En la bibliografía científica existe una amplia información sobre el uso de la catálisis heterogénea en la oxidación de compuestos orgánicos con peróxido de hidrógeno [4]. La Figura 2 recoge los trabajos científicos publicados en este tema hasta el año 2009. Sobre un total de 130 trabajos, se presenta la distribución por tipo de contaminantes tratados, fase activa empleada y soporte utilizado. Como puede observarse, los mayores esfuerzos se han centrado en la eliminación de fenol y diversos colorantes, utilizando, principalmente, hierro como fase activa. Entre los materiales más estudiados como soportes catalíticos se encuentran los óxidos de hierro, algunos óxidos mixtos y las zeolitas.

Desafortunadamente, hasta el momento, los sistemas catalíticos heterogéneos tampoco carecen de problemas. Las condiciones de operación utilizadas, así como algunos subproductos formados en el transcurso del proceso de oxidación, provocan la lixiviación de la fase activa, lo que se traduce en una baja estabilidad de los catalizadores [5]. Este inconveniente puede evitarse mediante el empleo de materiales carbonosos como catalizadores. En la bibliografía reciente [6-10] se

Figura 1
Esquema simplificado del proceso Fenton

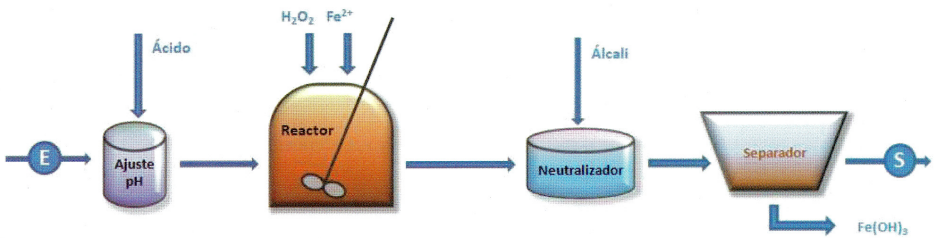
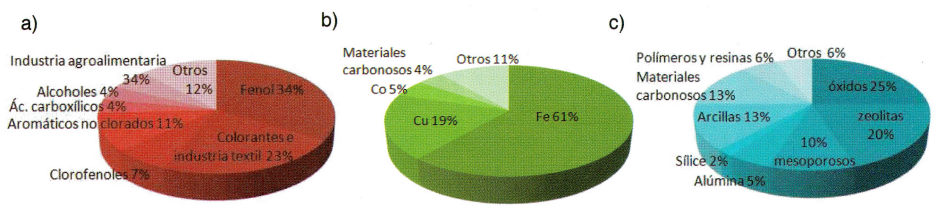


Figura 2
Publicaciones científicas sobre el proceso de oxidación húmeda con peróxido de hidrógeno y catalizadores sólidos clasificadas en función de: a) tipo de contaminante, b) fase activa y c) soporte. Fuente: ISI Web of Knowledge



ha estudiado el empleo de carbones activados, ya que tienen propiedades superficiales oxido-reductoras que promueven la descomposición del peróxido de hidrógeno a radicales hidroxilo [11], al tiempo que poseen una buena capacidad de adsorción de los compuestos orgánicos presentes en el agua [12]. Sin embargo, en las condiciones de reacción estudiadas, temperaturas 30-50 °C, presión atmosférica y cargas de contaminante bajas (DQO inferior a 2.000 mg/L), las conversiones alcanzadas resultan bajas (inferiores al 20% una vez consumido todo el peróxido de hidrógeno) [6,7, 9, 10].

En definitiva, la búsqueda de catalizadores sólidos estables para el tratamiento de aguas residuales industriales con cargas de DQO entre 2.000 y 20.000 mg/L, constituye todavía el caballo de batalla de los procesos Fenton heterogéneos. En el presente trabajo se estudia la aplicación práctica de distintos materiales carbonosos como catalizadores de bajo coste en la depuración de aguas fenólicas de carga media (DQO=3.000-15.000 mg/L) por oxidación con peróxido de hidrógeno en condiciones suaves (presión atmosférica y 80 °C). Se ha analizado la actividad catalítica de dichos materiales, así como su estabilidad, factor clave para su aplicación comercial.

1 PARTE EXPERIMENTAL

Se ha trabajado con cuatro tipo de materiales carbonosos: dos carbones activados, Merck (ref.:102514) y Panreac (ref.:121237), un negro de humo, Chemviron (ref.:0.45527), y un material con estructura equivalente al negro de humo pero exento de porosidad, preparado en nuestro laboratorio a partir de polietileno de baja densidad, que denominaremos PE [13]. Además, el carbón activado Merck se ha tratado térmicamente a 800ºC en atmósfera de nitrógeno con el fin de disminuir la cantidad de grupos oxigenados en su superficie (Merck-T800). El objetivo consiste en ensayar materiales con diferentes propiedades texturales (superficie específica y distribución de tamaño de poros) y químicas (cantidad y naturaleza de los grupos superficiales oxigenados), con el fin de analizar y tratar de entender cómo dichas propiedades afectan a la actividad y selectividad de estos materiales en su aplicación como catalizadores. Las técnicas empleadas, así como los parámetros medidos y los resultados obtenidos para cada carbón, se resumen en la Tabla 1.

Los experimentos de oxidación se realizaron en régimen discontinuo, en un reactor de vidrio que se cargó inicialmente con 45 mL de una disolución de fenol (1-5 g/L) y con 0,125 g de material carbonoso. Una vez alcanzada la temperatura de trabajo, 80ºC, se alimentaron 5 mL de una disolución de H_2O_2 (50-250 g/L) con el fin de aportar la cantidad de peróxido de hidrógeno equivalente a la dosis teórica estequiométrica para la oxidación completa de fenol a CO_2 y agua.

2 RESULTADOS Y DISCUSIÓN

La caracterización de los materiales, que se recoge en la Tabla 1, muestra, como era de esperar, una elevada superficie específica de los carbones activados (SBET superior a 900 m^2/g), mientras que el negro de humo y el sólido carbonoso PE tienen áreas superficiales de uno y dos órdenes de magnitud inferiores, respectivamente. El carbón Merck es más microporoso que el Panreac, que presenta una mayor contribución de mesoporos (Aext de 471 m^2/g en el Panreac vs. 175 m^2/g en el Merck). El negro de humo Chemviron presenta un desarrollo poroso muy inferior al de los carbones activados, mostrando básicamente mesoporos, mientras que el sólido carbonoso PE puede considerarse como no poroso.

Atendiendo al análisis de la naturaleza química superficial de estos materiales carbonosos por valoración ácido-base [9], el carbón activado Merck presenta un contenido mayor de grupos oxigenados ácidos y similar de básicos que el carbón activado Panreac. Por el contrario, el negro de humo y el sólido carbonoso PE no contienen oxígeno y, por tanto, no presentan grupos oxigenados en cantidades significativas. La naturaleza ácida/básica del negro de humo Chemviron es debida principalmente a la existencia de ácidos y bases de Lewis en su superficie. En el carbón Merck-T800 se ha reducido significativamente la cantidad de grupos oxigenados de naturaleza ácida por desorción a alta temperatura.

Con el fin de analizar la actividad catalítica de los carbones y su dependencia con las propiedades textu-

TABLA 1

CARACTERÍSTICAS DE LOS MATERIALES CARBONOSOS ENSAYADOS

Catalizador	Análisis textural		Análisis composición química						Análisis química superficial	
	Ads/des de N_2		Análisis elemental CHNS*						Valoración ácido/base	
	SBET (m^2/g)	A_{ext} (m^2/g)	C %	H %	N %	S %	Cen. %	O %	Centros ácidos (μeq H^+/g)	Centros básicos (μeq HO-/g)
Merck	973	175	89,3	0,9	0,5	0,6	4,0	4,7	626	450
Panreac	931	471	93,7	0,8	0,3	0,1	1,0	4,1	229	500
Chemviron	75	75	99,9	0,0	0,10	0,0	0,0	0,0	920	450
PE	3	-	99,4	0,4	0,0	0,0	0,2	0,0	n.m.	n.m.
Merck-T800	833	136	92,8	0,3	0,7	0,6	4,0	1,6	230	577

* Porcentaje másico de oxígeno (%O) estimado por diferencia (100-%C-%H-%N-%S-%cenizas).
nm: no medido

LA CONVERSIÓN DE FENOL ALCANZADA CON LOS DISTINTOS SÓLIDOS CARBONOSOS AUMENTA CON LA SUPERFICIE ESPECÍFICA

rales y químicas de éstos, se realizaron ensayos de actividad bajo las condiciones de operación fijadas (80 °C y 1 atm). En la Figura 3a se muestra la evolución temporal de la conversión de fenol durante las primeras 8 h de reacción con cada uno de los materiales ensayados. Además, se incluyen los resultados obtenidos en ausencia de catalizador. Todos los materiales fueron previamente puestos en contacto, en presencia de agitación, con una disolución de fenol (0,5 g de fenol y 1 g de carbón en 100 mL de agua) hasta llegar al equilibrio de adsorción, con el objetivo de minimizar la contribución de la adsorción en la desaparición de fenol observada en los experimentos de reacción.

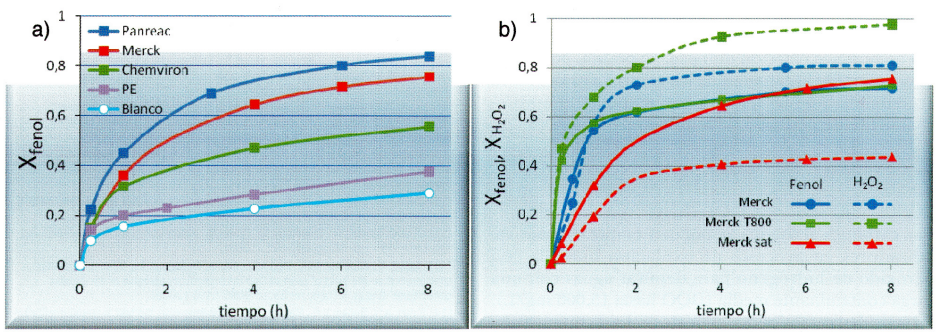
De acuerdo con los resultados mostrados en la Figura 3a, la conversión de fenol alcanzada con los distintos sólidos carbonosos aumenta con la superficie específica, al igual que la de peróxido de hidrógeno (resultados, estos últimos, no mostrados). El caso extremo es el del catalizador PE, con área prácticamente despreciable, que apenas promueve la reacción de descomposición del peróxido y, por tanto, no presenta actividad catalítica. En todos los casos, excepto con el carbón PE, se detectó cualitativamente la presencia de radicales hidroxilo mediante el método colorimétrico del azul de metileno [14].

El efecto de los grupos superficiales oxigenados se estudió a partir de los ensayos realizados con los carbones Merck y Merck-T800, sin ser sometidos previamente a saturación con fenol. La evolución temporal de la desaparición de fenol y peróxido de hidrógeno observada en presencia de estos materiales se muestra en la Figura 3b. Durante las dos primeras horas de reacción, es mayor la desaparición de fenol en presencia del carbón Merck-T800. En este periodo de tiempo, la desaparición de este reactante es principalmente debida al fenómeno de adsorción, como indicó la ausencia de intermedios de oxidación. Superado dicho periodo, predomina la reacción de oxidación, observándose en ambos casos la misma conversión de fenol. Por el contrario, la conversión de peróxido de hidrógeno se mantiene siempre por encima con el carbón Merck-T800. Estos resultados apuntan a dos conclusiones: i) que los grupos superficiales oxigenados que desorben hasta 800 °C no son los responsables de la actividad catalítica del carbón, ya que, en su ausencia, la descomposición de peróxido de hidrogeno está favorecida, y ii) el peróxido de hidrógeno se puede descomponer de manera no efectiva, ya que el carbón Merck-T800 favorece la descomposición de peróxido de hidrógeno y, sin embargo, esto no se refleja en una mayor conversión de fenol. Los productos de descomposición inocuos de peróxido de hidrógeno son oxígeno y agua, siendo el oxígeno inactivo en las condiciones de reacción como fue comprobado mediante un experimento llevado a cabo con un caudal de oxigeno de 100 mL/min.

Cuando la superficie del carbón se encuentra parcialmente ocupada por moléculas de fenol adsorbidas, como ocurre con el carbón Merck pre-saturado (Figura 3b), es posible aumentar la selectividad hacia la producción de radicales hidroxilo y aprovechar mejor el peróxido de hidrógeno, como demuestran los bajos valores de conversión de peróxido de hidrógeno observados con este carbón para similares conversiones de fenol (Figura 3b).

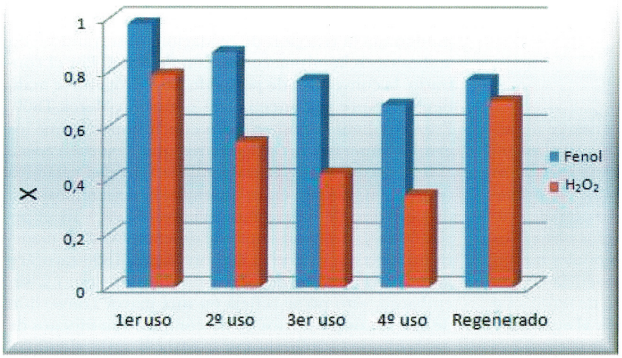
Un aspecto crucial para la comercialización de cualquier catalizador es su estabilidad. En el caso de los carbones activados, durante el transcurso de la reacción podrían ocurrir cambios en la composición química de su superficie, fenómenos de adsorción irreversibles o ensuciamiento de la superficie por algunos productos de oxidación [15]. Como consecuencia, la cantidad de centros activos podría reducirse progresivamente con

Figura 3
Actividad catalítica de a) materiales carbonosos y b) carbón activado Merck sometido a diferentes pretratamientos



Condiciones de operación de los experimentos de oxidación: T=80 °C, $C_{incial\ fenol}$ =5 g/L, $C_{incial\ H2O2}$ =25 g/L y C_{CAT}=2,5 g/L.

Figura 4
Estudio de estabilidad del carbón activado Panreac



T=80 °C, $C_{incial\ fenol}$=1 g/L, $C_{incial\ H2O2}$=5 g/L y C_{CAT}=5 g/L y t_R=4 h

el tiempo de uso del carbón, lo que conduciría a una disminución de la producción de radicales hidroxilo, responsables de la oxidación, y, por tanto, a pérdida de actividad del carbón. En la Figura 4 se muestran los resultados obtenidos, al mismo tiempo de reacción, en cuatro usos consecutivos del carbón Panreac. La conversión de fenol disminuye progresivamente al hacerlo la de peróxido, ésta última más afectada. Los análisis termogravimétricos del catalizador fresco y tras su cuarto uso revelaron la existencia de especies relativamente volátiles y oxidables en la superficie del carbón, cuya desaparición, cuando fueron sometidas a un flujo de oxígeno de 100 mL/min, comenzaba a temperaturas en torno a 150 °C y continuaba hasta temperaturas altas, a las que ya se observaba combustión del propio carbón. Se decidió llevar a cabo la regeneración térmica del catalizador a 250 °C, durante 20 h, en atmósfera de aire. El ensayo de actividad del catalizador regenerado (Figura 4) muestra una recuperación de la conversión de fenol, hasta valores similares a los obtenidos en el tercer uso, pero con un peor aprovechamiento de peróxido de hidrógeno, como indica su mayor consumo. Hay que tener en cuenta que durante el tratamiento térmico podría producirse la desorción de los grupos oxigenados más lábiles, como los ácidos carboxílicos, así como la incorporación de oxígeno a la superficie del carbón por reacción química. Se podría, por tanto, haber alterado la cantidad de los centros activos y/o su accesibilidad, de tal manera que empeore el aprovechamiento de peróxido de hidrógeno.

3 CONCLUSIONES

Los carbones activados se pueden emplear como catalizadores en procesos de oxidación húmeda con peróxido de hidrógeno para depurar aguas con una carga contaminante media (DQO hasta 15.000 mg/L). Su actividad catalítica depende de poder mantener una alta selectividad de la reacción de descomposición de peróxido de hidrogeno a radicales hidroxilo, de alta capacidad oxidante, e inhibir, en la medida de lo posible, la descomposición a oxígeno y agua. Para ello, se propone el bloqueo parcial de la superficie del carbón por la propia molécula de contaminante, lo que, a efectos prácticos, supondría someter al catalizador a una etapa de adsorción previa a la de reacción.

Con el uso, el carbón pierde actividad, pero puede regenerarse mediante un tratamiento térmico en atmósfera de aire a 250 °C. El grado de recuperación dependerá del efecto de este tratamiento sobre la selectividad del carbón en la producción de las especies radicalarias responsables de la oxidación. En cualquier caso, la conveniencia o no de dicha regeneración debe valorarse en función del coste del material.

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In: Focus on Catalysis Research: New Developments ISBN: 978-1-62100-444-8
Editors: Minjae Ghang and Bjørn Ramel

Chapter 9

EMERGING CATALYSTS FOR WET AIR OXIDATION PROCESS

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ABSTRACT

Wastewater treatment has reached a maturity state but the growing industrialization along with the more stringent environmental regulations demand an increasing dynamism in short and medium term. Accordingly, the existing technologies should improve in both versatility and efficiency and, in this sense, catalysts can play a prominent role. In this chapter, the authors offer a critical review of the catalysts currently investigated for the industrial wastewater decontamination by wet air oxidation. A survey of catalysts industrially implemented and academically investigated is presented and their nature and competitive features in activity and durability remarked. The current trend in the exploration of nanomaterials in the wet air oxidation field is highlighted. Updated research on nanotechnology-based catalysts, specially, carbon nanostructures and gold nanoparticles, is summarized and thorough discussed. Our recent results involving nanoscale gold particles are also included.

FUNDAMENTS

Wet air oxidation (WAO) is a well established technology for the removal of both organic and some inorganic pollutants from industrial process water and wastewater. It involves the oxidation of dissolved or suspended substances in aqueous phase using a gaseous source of oxygen, usually air, at high temperatures and pressures. The elevated temperatures are convenient to assure rapid oxidation and mineralization rates and the elevated pressures

are required to carry out the reaction in liquid phase and to enhance the solubility of oxygen in water (Mishra et al.,1995).

The WAO units typically run at 0.5-20 MPa and 400-700 K, with residence time from 10 to 120 min. Conversion of organics in these conditions ranges from 80 to 99%, and chemical oxygen demand (COD) reduction is completed by 60-90%. WAO is a technology with expertise in refineries, coke ovens, organic compounds production plants, pharmaceutical factories, pulp and paper mills, and textile and surface treatments plants (Cybulski, 2007). This wide array of industrial process water and wastewater illustrates the versatility of this technology, which is still more relevant, in the current context of frenetic industrial dynamism and stringent environmental regulations.

The flow diagram of a typical WAO plant is depicted in Figure 1. The wastewater is brought to the system pressure using a high pressure pump. Air is fed to the reactor using a compressor. Both streams are brought together and preheated to raise the operating temperature, by heat recovering from the effluent stream. The pressurized and hot inlet stream enters in the reactor where oxygen diffuses from the gas to the liquid and reacts with the pollutants in water. The bi-phasic effluent is cooled down first by the feed and then by cooling water, and subsequently disengaged in a separator. The off-gases can be expanded in a turbine to recover energy. The liquid phase can be directly discharged or most often subjected to a biological treatment.

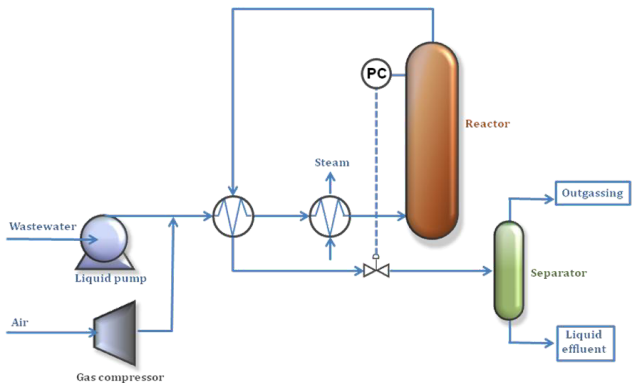

Figure 1. Schematic diagram of a wet air oxidation unit.

The oxidation of organic pollutants proceeds through a free-radical mechanism. Initially, the cleavage of the C-H bond occurs with formation of a free radical R·. This radical reacts with molecular oxygen to give an alkylperoxyl radical (ROO·). This reacts with another organic molecule (RH) producing the alkylhydroperoxyl species (ROOH) which is unstable and decomposes to intermediates with lower number of carbons (Cybulski et al., 2007).

The degree of oxidation depends on the temperature, oxygen partial pressure, residence time and the reactivity of the specific pollutant. The organic contaminants are either partially degraded into low molecular weight oxygenated compounds (*i.e.* maleic, fumaric, malonic, propionic oxalic, acetic and formic acids as well as methanol, ethanol and acethaldehyde) or mineralized into CO_2. Nitrogen is converted mostly to ammonia and also to nitrate and

elemental nitrogen. Halogens and sulphur are oxidized to inorganic halides or sulfates. Phosphorous oxidize to phosphates and chlorine compounds to HCl. Debellefontaine and Foussard (2000) reported the following mass balance with a heat value of 435 kJ/mol of oxygen consumed:

$$C_m H_n O_k Cl_w N_x S_y P_z + (m + 0.25(n - 3x) - 0.5k + 2(y + z)) O_2 \rightarrow$$
$$\rightarrow mCO_2 + 0.5(n - 3x) H_2O + xNH_3 + wCl^- + ySO_4^{2-} + zPO_4^{3-} + Q$$

In contrast to other thermal processes, WAO does not produce toxic gases *viz.* NO_x, SO_2, dioxins or furans.

WAO does not guarantee the complete destruction of the pollutants to carbon dioxide and water or to nitrogen. The mineralization occurs to large extent, but some innocuous by-products such as low molecular weight oxygenated compounds, *viz.* acetic acid, as well as ammonia are refractory to the oxidation. Extreme temperatures and rather long residence times would be required to increase the mineralization, factors that would make the process economically unsustainable. Therefore, WAO is most commonly conceived as a first step of a combined strategy in which the effluent from the oxidation is subsequently discharged into a conventional biological treatment plant (Scott and Ollis, 1995; Mantzavinos and Psillakis, 2004). Thus, the biodegradability of the exit stream along with the oxidation degree are the determining factors regarding the efficiency of the WAO process. Surprisingly, biodegradability and ecotoxicity tests of the WAO effluents have only been studied in the recent years (Santos et al., 2004a and b; Pintar et al., 2004; Mantzavinos and Psillakis, 2004; Rubalcaba 2007; Suarez-Ojeda 2007; Santos et al, 2009).

The constrain of WAO processes is the high capital costs associated to the high-pressure equipments and constructions materials (most oxidation by-products are corrosive under the reaction conditions, and then the use of special alloys is demanded) and the energy cost derived from operation at high temperatures and pressures. For this reason, the applicability of WAO is, in practice, limited to wastewater with an organic load content that makes the process autothermal. In general, WAO becomes practical for wastewaters with COD of at least 20.000 mg/L. The use of oxygen instead of air can improve the profitability, despite its higher cost (Prasad and Materi, 1990).

Nowadays, WAO is a proven technology with more than 200 industrial installations in operation, with the first commercial unit for the treatment of sulfite liquors being started in the late 1950s (Cybulski et al., 2007). Maugans and Ellis (2002) presented an extensive review of industrial WAO processes.

The efficiency of WAO (conversions and biodegradability of the exit stream) can be increased and the process energy demand simultaneously decreased by the incorporation of a catalyst. The catalyst is believed to participate in the activation of reactants by promoting the formation of the organic radical. Organic pollutant (RH) are adsorbed on the catalytic active sites and easily transformed to radical species (R·) by abstraction of the hydrogen through a redox reaction with the metal (Sadana and Katzer, 1974; Pintar and Leves, 1994).

As it happens with WAO, catalytic wet air oxidation (CWAO) is considered,for partial oxidation of pollutants into more biodegradably amenable intermediates, but now the presence of catalyst fairly minimizes the emission and allows the operation at significantly milder operating conditions and lower residence times. Hence, catalyst positively affects the

economics of the process oxidation. According to Levec (1997), the operating costs of the CWAO unit commercialized by Nippon Shokubai, are 1.5-3 times lower than those for a typical WAO.

CONVENTIONAL CATALYSTS IN WAO

The CWAO technology started in the mid-fifties in the United States (Moses, US 2690425). It implied the development of adequate catalysts and new reactor configurations. Several Japanese companies developed CWAO processes based on heterogeneous catalysis whereas in Europe, the focus was on the homogeneous. Table 1 summarizes reactor types, operating conditions, residence times and common catalysts of the current CWAO commercial units. Extensive description of these units has been published in several reviews (Kolaczkowski et al.,1999; Luck, 1996 and 1999, Silva 2009).

The commercial processes are mostly based on homogeneous catalysis (Cu^{2+}, Fe^{2+}). The few heterogeneous processes involve noble metal catalysts (Ru, Pd, Pt). The plants running with homogeneous catalysts need additional processing steps for the recovery and reuse of the metal, *i.e.* by some precipitation/separation technique (Ciba Geigy), which increases the operating cost. The supported noble metals exhibit higher activities but suffer from deactivation. They are vulnerable to poisons including polymers formed upon CWAO conditions and also lose activity because of the metal oxidation. This sensitivity to deactivation can be reduced by the adequate choice of the support (Cybulski et al., 2007).

Table 1. Reactors, operating conditions, residence times and catalysts in commercial catalytic wet air oxidation processes.

Commercial Units	Reactor	T (K)	P_T (MPa)	t_R (h)	Catalyst
Loprox	Bubble column	313-473	0.5-2	1-3 h	Fe^{2+} and H_2O_2 promoter
IT Enviroscience	Stirred Tank	438 - 548	1.2-7	0.5-2	Br^-, NO_3^-, Mg^{2+}
Ciba-Geigy	Bubble column	573	20	3	Cu^{2+}
Orcan	-	120	0.3	-	Fe^{2+} and H_2O_2 promoter
Kurita	-	170	-	-	Supported Pd
ATHOS[§]	-	235	4	-	Cu^{2+}
NS-LC	Trickle-bed	433-543	0.9-8	1	Pt-Pd/TiO_2-ZrO_2 (monolith), Ru/CeO_2 (pellets)
Osaka Gas	Trickle-bed	523	7	0.5	Fe, Cu, Co or Ni/ Ru, Pd, Pt or Au /TiO_2 or ZrO_2

[§] treatment plant for sludge.

Investigation stimulated to search for active and stable catalysts capable of perform the oxidation of a particular kind of wastewater at milder operating conditions has resulted in the proliferation of a vast literature in the CWAO field since the seventies. More than 700 entries can be found searching with the topic *catalytic wet air oxidation* in the ISI Web of Knowledge. This literature survey is classified in Figure 2 attending to different general

aspects: sort of document in which the information is provided (a), model pollutants and real wastewater used as inflowing streams (b) and nature of the investigated catalysts (c).

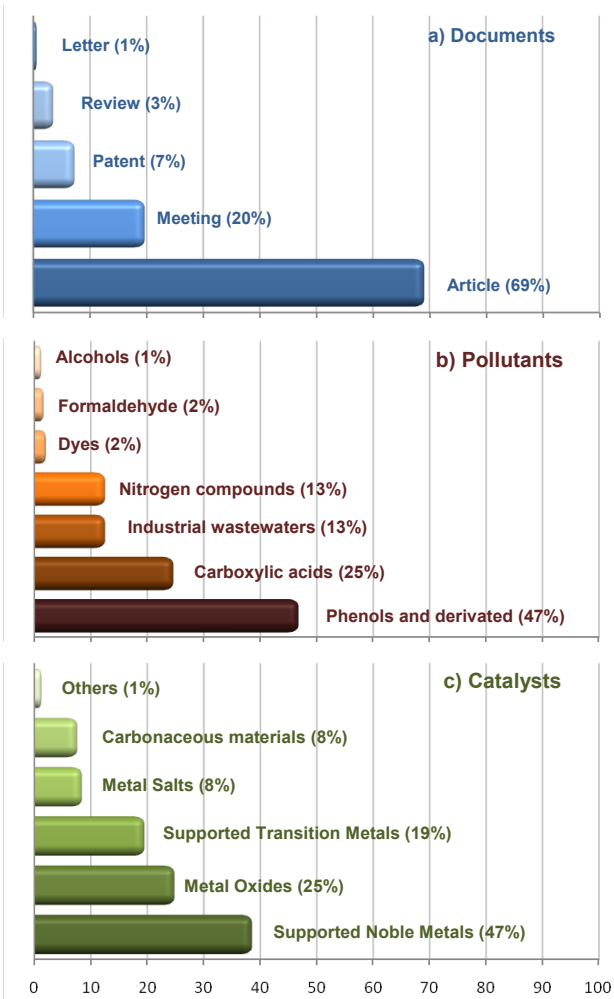

Figure 2. Literature generated in the CWAO field distributed by sort of documents (a), pollutants (b) and catalysts (c) studied. Source: *ISI Web of Knoweldge.*

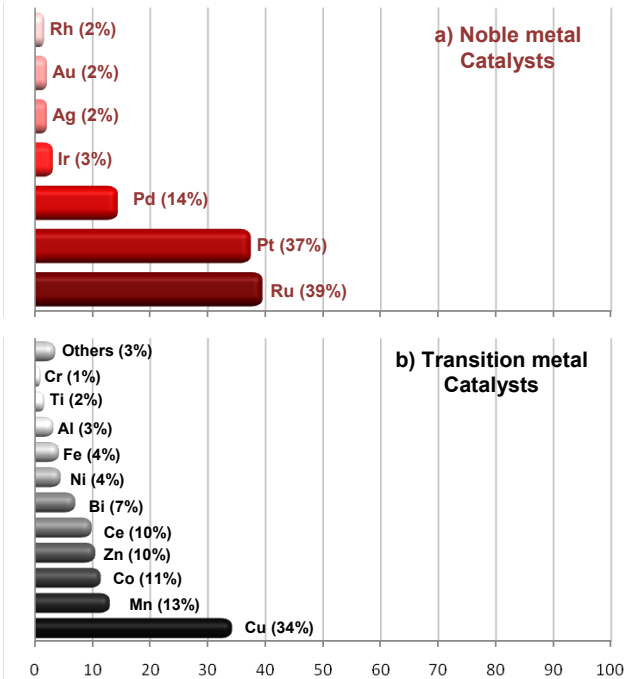

Figure 3. Distribution of papers devoted to noble (a) and transition metal (b) catalysts.

The information deduced from this Figure 2a reveals that only 7% of the documents are patents, in spite of the important proliferation of divulgative documents (articles, meetings, reviews and letters). The patents basically claim for catalysts and operating conditions for the oxidation of model pollutants. These figures manifest the difficulty in the development of suitable catalysts.

Phenols and derivates (chlorophenols and nitrophenols) have been preferentially used as model pollutants followed by carboxylic acids (Figure 2b), the most resistant compounds to the wet oxidation and also by-products in the oxidation of most organic compounds. Nitrogen compounds raised researcher's interest coinciding with the application of CWAO for the treatment of agricultural wastewater polluted by ammonia. An extensive review about the removal of ammonia and nitrogen-containing compounds has been published by Oliviero et al., (2003). Dedication to real wastewater started from the nineties and due to the employ of wastewater of different origin (paper, petrochemical, dye industries, olive processing, wine distilleries etc.) has been possible to be more concise about catalyst durability.

Four types of catalysts tested: (supported) noble metals, (supported and unsupported) metal oxides, metal salts and carbon materials (Figure 2c). The distribution of papers devoted to the different noble and transition metals investigated is complied in Figure 3. Ruthenium, platinum, palladium and copper are the most intensively tested because of their high activity. A comprehensive survey of investigations on catalysts for CWAO processes is provided in

the reviews of Matatov-Meytal and Sheintuch (1998), Imamura (1999), Yang et al. (2002), Pirkanniemi and Sillanpää (2002), Bhargava et al. (2006), Levec and Pintar (2007) and Cybulski (2007). In these works, lists of the catalysts used in the oxidation of different compounds along with the operating conditions and reactor types are provided.

Noble Metals

Supported noble metals (ruthenium, platinum, palladium, iridium, silver, and rhodium) are the most studied because of their exhibited high activities, particularly with carboxylic acids. As a consequence, the mineralization to CO_2 and H_2O of high weight molecules such as phenol, *p*-coumaric acid and aniline is usually higher. Different rankings of activity have been reported depending on the model pollutant tested and the metal/support combination. For instance, Okitsu et al., (1995) studied the oxidation of *p*-chlorophenol with noble metals on alumina or titania and found the following activity order: Pt >> Pd > Ru > Rh >Ag. Similar conclusion was later obtained by Qin et al. (2001) when using activated carbon, alumina and ceria as supports. Immaura (1988), compared the activity of the noble metals on alumina, ceria, titania and zirconia in the oxidation of PEG-200, and the activity in terms of TOC followed: Ru = Rh = Pt > Ir> Pd. Barbier et al. (2005), reported for the oxidation of phenol and with ceria as support: Ru > Pd > Pt. Conversely, Trawczýnski (2003) found also for the oxidation of phenol but with carbon black composites (CBC) supports, a different ranking: Pt > Pd > Ru >> CBC. These results evidence the importance of some supports such as ceria and carbon, which results to be catalytically active in the oxidation (Figure 2c and Figure 3b).

In general, noble metal catalysts are comparably more expensive than the rest of catalysts reported, and specially at the high metal loads (1-5wt%) used in the CWAO. In this context, the durability of the catalyst gains relevance. Precious metals are resistant to leaching but more sensitive to poisoning when halogen-, sulphur- and phosphorus-containing compounds are the pollutants. They also deactivate by the fouling originated by the deposition of polymers formed upon reaction. Metal oxidation can also take place leading to a loss of active sites. Different strategies have been studied to increase their longevity: *i)* the use of the appropriate wastewater, *ii)* the use of fixed-bed reactors instead of tanks to employ low liquid-solid ratios in order to reduce the formation of the polymers in the liquid phase (Pintar and Levec, 1992) and *iii)* the addition of small amounts of hydrogen to the gas stream with the aim of maintaining the metallic active sites and reducing the formation of polymer (Kim et al., 2003 and 2005).

Metal Oxides

Supported and unsupported metal oxides (copper, manganese, cobalt, zinc, cerium, and bismuth) have been also tested. The following ranking in the activity was reported by Kochetkova et al., (1992) in the oxidation of phenol: CuO > CoO > Cr_2O_3 > NiO > MnO_2 > Fe_2O_3 > YO_2 > Cd_2O_3 > ZnO > TiO_2 > Bi_2O_3. Copper oxide was found to be the most active one. The intensive literature devoted to this catalyst and the main goals achieved has been recently reviewed by Cybulski (2007). Its principal limitation comes from the insufficient

durability caused by the acidic pH of the media, inherited to the CWAO, which provokes the metal leaching. Nevertheless, the low cost of these catalysts compared to noble metals has stimulated their investigation even at the cost of lower activity. The investigation on the improvement of the catalytic performance of the metal oxides led to the development of composite oxide catalysts (Ce/Al, Mn/Ni, Mn/Ce, Co/Bi, Co/Mo, Cu/Zn, Cu/Fe, etc.). Copper catalysts with basic active sites like bismuth, cobalt and manganese exhibit relative high activities in the oxidation of carboxylic acids and also reduced the copper leaching (Cybulski, 2007).

The most effective means to prevent leaching accounts for modifications on catalyst preparation. As an example, Hocevar et al. (1999) prepared the mixed $Ce_{1-x}Cu_xO_{2-d}$ by precipitation and sol-gel methods and copper was much less soluble than the copper oxide dispersed on ceria and prepared by impregnation. Alejandre et al. (1998) selected the appropriate metallic phase, *viz.* spinel phase, which resulted to be stable by modifying the calcination temperature. The operating conditions, in particular the pH of the inlet wastewater, can be also manipulated to avoid leaching. The work of Santos et al. (2005a) demonstrated that the strategy of buffering phenolic wastewater to basic values (pH=8 with bicarbonate) succeeds in maintaining the stability of the CuO/Cr_2O_3/graphite catalyst (copper was neither leached nor fouled), though, in addition, copper selectivity is affected. Bicarbonate anions are scavengers of phenol peroxide radicals and consequently different aromatic by-products to those usually detected at acidic conditions are formed. Also, lower reaction rates were observed which was explained by the absence of the homogeneous contribution to the overall oxidation reaction.

Metal Salts

Copper, as well as, niquel, iron, cobalt, chromium and manganese salts were first investigated. The supremacy of the copper activity is exemplified in CIBA unit that uses $CuSO_4$ as catalyst. Due to the oxidizing conditions, the active metals are usually in their highest oxidation states. Their activity is affected by the counteranions (Immamura, 1982), the pH of the reaction media and the nature of the pollutant and by-products formed (Santos et al., 2005b). All these factors ultimately affect the metal solubility.

Carbon Materials

Carbon materials such as activated carbons, graphites and carbon blacks are active catalysts. Stuber et al. (2005) reviewed their application for CWAO processes. The supremacy in the number of papers using activated carbons over the rest of carbon materials was evidenced in this work. Activated carbons are relevant catalysts because of their high adsorption capacity towards several compounds, in particular aromatic compounds and polymers, which are non-biodegradable and ecotoxic. The adsorption contribution to the removal of these compounds increases the efficiency of the treatment when activated carbons are used. The activity of the activated carbon is attributed to the concentration of oxygen bearing functional groups present on the surface. In general, the mild conditions required in order to avoid their partial combustion (T< 433 K and p_{O2}<0.9 MPa, Mundale et al. 1996)

invites to use metal active phases, such as noble metals (Ru, Pd, Pt) and metal oxides (Fe_2O_3 and CuO_2) or to use a promoter such as hydrogen peroxide (Quintanilla et al. 2010 and Rubalcaba, 2007) to enhance the activity. Quintanilla et al. (2010) demonstrated the better performance (initial rates, oxidation and mineralization degrees and ecotoxicity removal) in presence of that promoter than iron. Figure 4 shows those results by representing the removal curves of phenol, TOC and ecotoxicity, the latter expressed in toxicity units (TU).

Activated carbons are physical and chemically modified upon reaction. Their surface evolves as a consequence of the oxidation treatment and the pollutant adsorption. The specific surface area significantly reduces and the number of oxygenated surface groups importantly increases but these changes do not affect their catalytic activity (Quintanilla et al., 2007). As an example, the activity of Fe/activated carbon catalyst was unperturbed during 200 h of time on stream in CWAO of phenol at 400 K and 0.8 MPa (Quintanilla et al., 2007). This adequate durability makes them very attractive catalysts for CWAO.

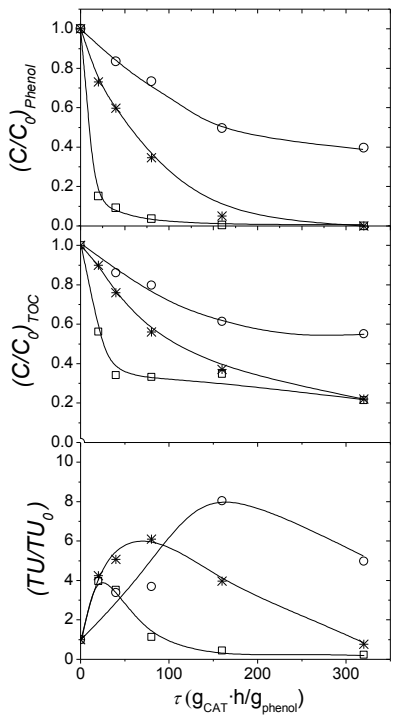

Figure 4. Catalytic activity and ecotoxicity of the effluent in the CWAO of phenol in a trickle-bed reactor over activated carbon (○), 2.5wt% Fe/activated carbon (*) and activated carbon plus H_2O_2 promoter (□). Reaction conditions: C^{0}_{phenol} =1 g/L, Q_{O2}=91.6 NmL/min, w_{cat}=2.5 g, T=400 K, p_{O2}=8 atm. Lines to guide the eye.

Pirkanniemi and Sillanpää (2002) reviewed the supports tested in CWAO. The most common are metal oxides, *viz.* TiO_2, Al_2O_3, ZrO_2 and CeO_2, and activated carbons (Duprez et al., 1996; Cao et al., 2003; Oliviero et al., 2000; Gomes et al., 2000, 2002a, 2002b; Quintanilla et al., 2006). As aforementioned, ceria and carbon are the most interesting supports since improve the catalyst activity. Ceria-containing catalysts are stable and enhanced textural and catalyst redox properties at low temperatures (Trovalrelli et al., 1999; Oliviero et al., 1999; Cylbuski, 2007). Activated carbons are low cost materials and interesting candidates when the wastewater (sort and amount of pollutant) admits mild oxidation conditions.

The experience gathered on the application of the described catalysts, compiled in Figures 2c and Figure 3, in the remediation of a wide array of wastewater (Figure 2b) points out that the selection of the most adequate catalyst is ultimately decided by the nature and amount of the pollutant. The starting hazardous compound and the reaction by-products are decisive for the catalyst durability for several reasons: they can be prone to polymerize giving rise to catalyst fouling and they can contribute either to decrease the pH or form complexes with the metal (Santos et al., 2005; Perathoner and Centi, 2005), promoting, in both cases, the leaching of the active phase in heterogeneous systems or modifying the solubility of the metal salt in homogeneous systems, thus negatively affecting the activity. As an example, two different works came out with a different conclusion regarding the stability of a particular catalyst, $CuO\text{-}ZnO/Al_2O_3$. This catalyst was applied in the CWAO of *p*-coumaric acid (Mantzavinos et al., 1996) and formaldehyde (Silva et al., 2003) at not very different operating conditions. Only in the former, an obvious elution of copper, zinc and aluminium was detected and the homogeneous contribution to the overall oxidation reaction could not be discarded. Therefore, the final selection of catalysts will be dictated by the nature of the particular industrial wastewater to decontaminate.

With the above background, one can deduce that researches investigating in the CWAO field still need to face significant challenges: *i)* searching for economic and environmentally friendly catalysts and *ii)* the optimization of catalyst activity while maintaining a high stability. The persecution of these goals has resulted in the exploration of nanomaterials for catalysts in the CWAO technology.

NANOTECHNOLOGY IN WET AIR OXIDATION

The current trends in CWAO explore the use of nanomaterials. The application of nanotechnology in the water field is expected to produce environmental benefits in terms of water management and treatment by improving filtering, decontamination, desalination, conservation, recycling, analysis and monitoring of sewerage systems. The investigation about the application of nanotechology in water treatments can be found in recent reviews (Theron et al. 2008; Derhmendra et al., 2008; Ong et al., 2010). There, filtration and adsorption are evidenced as the dominating application so far. In addition, dechlorination and disinfection by photocatalysis are also processes gaining relevance. Chemical oxidation was not mentioned which reveals the incipient interest of nanomaterials in environmental oxidation technologies.

Table 2. Emerging catalysts in catalytic wet air oxidation treatments.

Reference	Catalyst	Pollutant	poll./cat. (mol:mol)	*T* (K)	*P* (MPa)	Results
Gomes et al. 2004	1% wt. Pt/MWCNT	Aniline	39.3	473	0.7	$X_{aniline}$ = 77% (1 h), 98.8% (2 h)
	1% wt. Pt/AC		39.3			$X_{aniline}$ = 95% (1 h), 100% (2 h)
	1% wt. Pt/CX		39.3			$X_{aniline}$ = 98% (1 h), 100% (2 h)
García et al. 2005	1% wt. Pt/MWCNT	Aniline	39.3	473	0.7	$X_{aniline}$ = 99.4 %, X_{TOC} = 78.3% (2 h)
	1% wt. Pt/AC	Aniline	39.3			$X_{aniline}$ = 100 %, X_{TOC} = 94.5% (2 h)
	1% wt. Pt/MWCNT	Azo dye SG	2.8			X_{dye} = 99.5%, X_{TOC} = 21.2% (2 h)
	1% wt. Pt/MWCNT	Azo dye ERB	8.1			X_{dye} = 99.5%, X_{TOC} = 78.1% (2 h)
	1% wt. Pt/MWCNT	Azo dye C2R	8.4			X_{dye} = 100%, X_{TOC} = 63.5% (2 h)
	1% wt. Pt/MWCNT	Textile wastewater	-			X_{TOC} = 51.2%, X_{COLOR}=100% (2 h)
García et al.2006	1% wt. Ru/MWCNT	Aniline	20.3	473	0.7	$X_{aniline}$ = 100%, X_{TOC} = 80.8% (45min)
	1% wt. Ru/AC		20.3			$X_{aniline}$ = 100%, X_{TOC} = 96.4% (45min)
Ovejero et al. 2006	1% wt. Pt/N-MWCNT	Aniline	-	473	0.42	$X_{aniline}$ = 62.4%, X_{TOC} = 55.3% ($0.03h^{-1}$)
						$X_{aniline}$ = 97%, X_{TOC} = 85%
	1% wt.Pt/AC		-			($0.03h^{-1}$)
	1% wt. Cu/N-MWCNT		-			$X_{aniline}$ = 60.1%, X_{TOC} = 57.5% ($0.03h^{-1}$)
	1% wt. Ru/N-MWCNT		-			$X_{aniline}$ = 45.6%, X_{TOC} = 43.2% ($0.03h^{-1}$)
Yang et al. 2008	MWCNT	Phenol	0.0796[§]	433	2	X_{Ph} = 100%, X_{TOC} = 100% (2 h)
Rodríguez et al. 2010		Methylene				
	3% wt. Fe/MWCNT	Blue	0.0031	413	0.88	X_{TOC} = 35%, X_{COLOR} = 82% (2.5 h)
	3% wt. Cu/MWCNT		0.0035			X_{TOC} = 40%, X_{COLOR} = 90% (2.5 h)
Rodríguez et al. 2008		Textil				
	3% wt. Cu/CNF	Wastewaters	157.8	413	0.88	X_{TOC} = 74.1%, X_{COLOR} = 97% (3 h)
	3% wt. Cu/AC		157.8			X_{TOC} = 71.5%, X_{COLOR} = 90% (3 h)
Taboada et al. 2009	2% wt. Pt/CNF	Phenol	-	453-513	1	Catalyst deactivation
	2% wt.Pd/CNF		-			
	2% wt.Ru/CNF		-			
Soria Sánchez et al. 2009	1% wt. Fe acetylacetonate/CNF	Phenol	27.9	413	2	X_{Ph} = 100 %, X_{TOC} = 90% (2.5 h)
Sousa et al. 2010	CNF	Aniline	0.0901[§]	473	0.7	$X_{aniline}$ = 95 %, X_{TOC} = 90% (5 h)
	Carbon foam		157.8			$X_{aniline}$ = 78 %, X_{TOC} = 77% (5 h)
Gomes et al. 2008	CX	Anilina	0.0288[§]	473	6.9	$X_{aniline}$ = 99%, X_{TOC} = 86% (5 h)
Apolinário et al. 2008						
	CX	MNB,	0.0006[§]	473	0.69	$X_{DNT, TNP}$ > 90%, X_{TOC} = 80%(2 h)
		DNP	0.0020[§]			
		TNP	0.0006[§]			
Besson et al. 2003	5% wt. Au/TiO_2	Succinic acid	50.0	463	0.69	$X_{succinic}$ = 88% (6 h)
Milone et al. 2006	3.8% wt. Au/CeO_2	*p*- Cumaric acid	4.7	353	0.42	X_{TOC} = 85% (2.5 h)
Levi et al. 2008	Mn-Ce (Nanocasted)	Aniline		413	1	$X_{aniline}$ = 100%, X_{TOC} = 90% ($5\ h^{-1}$)
Yang et al. 2007	$LaCoO_3$ perovskite	Salycilic acid	0.3	383	0.5	X_{COD} = 85% (2 h)
Royer et al., 2008	$LaFeO_3$ and $LaMnO_3$	Stearic acid	1.4	473	2	Pollutant: X_{LaFeO3} = 65%, X_{LaMnO3} = 60% (3 h)
Zhang et al., 2009	$Zn_{1.5}PMo_{12}O_{40}$ nanotubes	Safranin-T	0.01	298	0.1	$X_{Safranin}$ = 90% (35 min)
Zhao et al. 2010	$[(C_nH_{2n+1})N(CH_3)_3]^{3+}{}_xP$ $V_xMo_{12-x}O_{40}$	Phenol	0.8	298	1	X_{Ph} = 95,3 %, X_{COD} = 98,5 % , X_{TOC} = 93% (1.5 h)

MWCNT: multi-walled carbon nanotube; AC: activated carbon; CX: carbon xerogel. [§] per mol of carbon.

Based on the literature, carbon nanostructures, *viz.* nanotubes, nanofibers and xerogels, and gold nanoparticles can be benchmarked as the most studied nanomaterials. By taking advantages of their extraordinary physical, chemical and electronic properties, they represent, along with the zero-valent iron nanoparticles (Theron et al., 2008), the first generation of nanoscale environmental technologies. The exciting results provided by carbon nanostructures (Ong et al., 2010) and gold (Bond et al., 2006) when they are exploited as catalysts in the hydrodechloration technology, *i.e.* removal of trichloroethene, one of the most common hazardous groundwater pollutants, has recently opened interesting opportunities in water decontamination technologies..

The recent research carried out on the catalytic applications of both carbon nanostructures and gold in WAO processes is collected in Table 2. As can be seen, carbon nanostructure studies have proliferated faster than those based on gold. The reasons point out to *i)* the existing large-scale production of the carbon nanostructures, which allows using commercial ones, while gold catalysts are usually home-made, *ii)* the modest number of factors affecting the activity of carbon nanostructures, which is preferentially ascribed to the surface chemistry, *iii)* the better knowledge of the carbon than gold chemistry. The activity of gold is still unclear and many aspects such as the preparation method, particle size, gold-support interaction and the nature of the supports are crucial for the gold nanoparticle activity, and finally, *iv)* the longer durability of carbon nanotubes than gold nanoparticles during oxidation.

The major aspects of carbon nanostructures and gold catalysts gathered along the short experience on their application in CWAO processes (Table 2) are next discussed.

Carbon Nanostructures

The potential characteristic that has encouraged the application of carbon nanostructured materials in CWAOs is their high external surface areas. The mesoporous surface provides an efficient surface contact between the reactants and the active sites, which is especially important in liquid-phase reactions where the mass transfer phenomenon becomes very significant. The carbon nanostructures are mostly used as catalytic supports, though they exhibit activity after activation (Yang et al., 2008). The activation consists in the chemical modification of the surface nanotubes/nanofibers usually by wet chemistry methods in which HNO_3 and HNO_3/H_2SO_4 are used as oxidants. As a result, functional groups such as carboxylic (-COOH), carbonyl (-CO) and hydroxylic (-OH) are formed on the surface of nanostructure. These oxygenated groups favor the adsorption of metal precursor and act as nucleating sites during the formation of the metal sites. Functionalization also enriches the reactivity of the nanostructures and modifies their wetting characteristics. The proper wetness is vital to avoid direct exposition of the carbon surface to oxygen in the gas stream and the consequent gasification of the carbon nanostructures. Taboada et al., (2009) experienced that the gasification in non-functionalized carbon nanofibers supporting noble metals (Ru, Pt and Pd) in the oxidation of phenol in a trickle-bed reactor.

The work of Yang et al., (2008) is the only one so far studying the applicability of bare carbon nanotubes as catalysts. The functionalized multi-walled carbon nanotubes (MWCNT) exhibited both high activity (97.2% and 77% phenol and TOC conversion, respectively, in 2 h of reaction) and good stability in several running cycles in the CWAO of phenol. The absence of some toxic by-products typically found in the phenol oxidation route, such as catechol and

p-benzoquinone, assists the potentialities of carbon nanotubes in the CWAO treatment of phenolic wastewaters.

As was previously commented, carbon nanostructures are usually explored as supports for preparing efficient solid catalysts. As shows Table 2, the active phases are noble metals, Ru, Pt and Pd (Gomes et al. 2004; García et al., 2005; Taboada et al. 2009) and metal oxides, Cu and Fe (Ovejero et al. 2006; Rodríguez et al., 2010). A global analysis of these works, fundamentally applied to the oxidation of aniline, induces that CWAO is efficiently performed using metal/carbon nanostructures catalysts. However, outstanding catalytic properties comparing to conventional catalysts, in particular activated carbon-based catalysts, are not observed (Garcia et al., 2005 and 2006; Gomes et al., 2004; Rodriguez et al., 2008). In fact, the mineralization degree achieved with activated carbons is usually higher because of their higher adsorption capacity that contributes to overestimate the activity. Durability of the carbon nanostructures is also an aspect to be refined. Leaching of Ru and Cu has been reported (Garcia et al., 2006; Rodriguez et al., 2008) suggesting a weak metal-support interaction. On this regard, the recent work of Soria-Sanchez et al. (2009) reports about an elegant alternative to the usual wet impregnation method selected for the metal immobilization on the nanotubes/fibers. The novel method consists in the preparation of Fe/carbon nanofiber catalysts by the anchoring of iron through complexation of iron ions on the acetylacetonate functional groups created on the functionalized carbon nanofibers. These catalysts demonstrated their good activity and stability in successive runs.

In addition to carbon nanotubes and nanofibers, xerogels have also been used as support (Gomes et al., 2004) and catalyst (Apolinario et al., 2008). The novel work of Gomes et al., (2004) comparing the activity of platinum supported on xerogel, activated carbon and nanotubes demonstrated that Pt/xerogel provides higher aniline removal and similar mineralization than Pt/carbon in contrast to the lower performance of Pt/nanotubes. This work opened the door to the exploitation of theses materials in CWAO. Xerogels have also been used as catalysts for the oxidation of nitrophenols in water at low concentrations (Apolinario et al., 2008). The activity was high (almost complete conversion of nitrophenols and 78% TOC conversion in 30 min) but with a contribution of adsorption higher than 50% in the pollutant removal. The xerogel stability upon oxidation is promising (MM) but long-term experiments are still required.

In conclusion, the results reported confirm the potentialities of the new carbon materials for the development of catalysts for CWAO but there is still a significant scope for further research and innovation.In fact, conclusive results on the application with real wastewaters, deactivation vulnerability and biodegradability of the effluents are required for a cost-efficiency evaluation. Efforts should be made to optimize catalyst preparation and reaction conditions to enhance efficiencies and prevent deactivation. The use of these carbon nanostructures as catalysts without a metal active phase can be a reasonable solution to gain in stability even at the expenses of lower activity.

Gold Nanoparticles

The work carried out with supported gold catalysts is gathered in a few papers (Besson et al., 2003; Milone et al. 2006; Trana et al., 2008). Wastewater containing different organic pollutants has been tested in these studies (see Table 2). Nitrogen-bearing pollutants are also

good candidates as demonstrated by the Nippon Shokubai patent (JP 06142660 A) for the treatment of wastewater containing this type of compounds with an oxide catalyst on which gold and optionally platinum are supported.

Besson et al. (2003) were the first to show the applicability of gold in CWAO. They evaluated the performance of Au/TiO_2 catalysts in the oxidation of succinic acid at 463 K and 2 MPa. In this work, several catalysts were prepared by deposition-precipitation following different protocols with the aim of synthesis selected-size nanoparticles. It was demonstrated that the gold activity was higher as the particle size decreased. The 2 nm particles were the most active, exhibiting a TOF value of 16 h^{-1} and complete conversion after 6 h of reaction. Nevertheless, the activity of Ru/TiO_2, the noble metal catalyst used for comparison, was superior, achieving complete conversion of succinic acid after 3 h at a higher pollutant/gold molar ratio. In addition, the gold activity decreased in a second run, the initial rate being reduced from 9.7 to 2.3 $mol_{succ}/mol_{Au}/h$. No leaching of gold was detected but sintering of the nanoparticles, from 2 to 4 nm, was observed. Analysis of the carbonaceous deposits on gold would be required for further conclusive knowledge of the causes of deactivation. Further studies carried out by the same research group (Trana et al., 2008) proved the activity of Au/CeO_2 catalysts in the oxidation of acetic acid. The catalyst was prepared by deposition-precipitation with urea and subsequently subjected to two alternative thermal treatments, calcination at 773 K in air or reduction at 573 K in H_2 atmosphere. The different distribution of gold species resulting on the ceria supports combined with the activity measurements demonstrated that Au^0 species is required to achieve a high catalytic performance. The catalyst showed aging due to sintering.

Milone et al. (2006) did not succeed in the preparation of Au/CeO_2 catalysts by coprecipitation and deposition-precipitation. According to XRD analyses, gold nanoparticles were only present in the catalysts prepared by coprecipitation, and their average size was 18.6 nm. The presence of gold in none case increased the own activity observed with ceria relative to *p*-cumaric acid conversion. The slight increase in the effluent TOC conversion was explained by the carbonaceous deposits formed on the catalyst surface induced by the presence of gold.

The above results state the activity of immobilized gold nanoparticles in the oxidation of carboxylic acids and also their vulnerability to deactivation. Therefore, CWAO is a fertile area for the application of gold catalysts. In this line and considering the huge variety of wastewater, the previous concern of our research group about the application of gold in CWAO was related to the catalyst versatility. For this, we selected alcohols, phenols and anilines as pollutants in our study. They are less refractory to the oxidation than carboxylic acids, fact that allows the use of milder operation conditions, which is expected to prevent to some extend, the gold sintering.

Two commercial catalysts with different average particle size were tested: 0.9wt%Au/Al_2O_3 (Au_{dp}=1.48±0.02 nm; Mintek, batch: BC17) and 0.8wt%Au/C (Au_{dp}=10.5 nm; World Gold Council). The supports were selected based on the previous works of Prati and Rossi (1998) in which these catalysts were successfully tested in air-oxidation of polyhydroxylated molecules in aqueous basic solutions. The pollutants selected were all aromatic compounds: benzyl alcohol, phenol and aniline. The oxidation experiments were carried out in a slurry reactor at 398 K and 0.6 MPa. The reactor was initially charged with 0.5 g of solid and 200 mL of 1g/L of pollutant solution at pH=10 (adjusted with NaOH) and a continuous flow of oxygen fed to the reactor.

Figure 5a provides the time-evolution of target pollutant, TOC and COD conversions in presence of Au/Al_2O_3 catalyst. As observed, the 1.48 nm particle sizes on alumina are active in the oxidation of both benzyl alcohol and phenol. Results with respect to aniline are not provided in the figure because gold was revealed as slightly active catalyst in the oxidation of this compound since similar conversions as in the blank experiment were obtained ($X_{aniline}$,$X_{TOC,}$ X_{COD} = 24, 22, 11% with Au/Al_2O_3 after 3 h of reaction whereas 19, 16, 8% were observed in the blank experiment). Therefore, gold activity varies attending to the nature of the target pollutant. The benzyl alcohol-gold system provides better results that the phenol-gold whereas aniline-gold system is scarcely active. The lower reactivity of phenol is in line with the results of Tsunoyama et al. (2006) for the air-oxidation of *p*-hydroxybenzyl alcohol on gold nanoparticles in solution, where this alcohol was oxidized to the corresponding aldehyde without altering the phenol group. Complete conversion was achieved for benzyl alcohol whereas only a 25% of phenol was converted after 3 h of reaction. Similar differences are also observed in TOC and COD conversions.

The different gold activity can be induced by the different pollutant-gold interaction. Oxygen atoms coordinate more predominantly than nitrogen on gold (Bonet et al., 2000). We do not discard that the site occupation by water molecules (Yang et al., 2008) could also contribute to the poor affinity between gold and aniline. In the case of alcohols and phenols though both molecules containes a hydroxyl group a different interaction with gold is expected.

Reviewing the extended literature on the oxidation of benzyl alcohol over gold catalysts in organic solvents, it is generally accepted the formation of the gold-benzyl alcoholate species which evolves to more oxidized products, typically benzaldehyde, via β-hydrogen abstraction and without the participation of the oxidant, which eventually will regenerate the active site (Mallat and Baiker, 2004; Abad et al., 2008; Brink et al., 2000). In the case of phenols, the above mechanism cannot be assumed because of the absence of the β-hydrogen in the phenol molecule. By electrochemical analysis, phenol has been demonstrated to be covalently adsorbed on gold electrodes by the oxygen atom and weakly adsorbed by the aromatic ring (Lezna et al., 1991), a similar situation could be ascribed in the case of gold nanoparticles. Therefore, we speculate that the phenol chemisorption on gold *vs.* the gold-alcoholate complex formation dictates the lower oxidation rate observed when phenols instead of alcohols are the pollutants in CWAO processes over gold catalysts. To obtain experimental evidences on the different interaction between the target organic molecules and gold, experiments under inert atmosphere were performed for each individual compound and Au/Al_2O_3. The results show that the removal of benzyl alcohol was only slightly favored than that of phenol (40 g of benzyl alcohol *vs.* 35 g of phenol per gram of gold disappeared after 24 of pollutant-gold contact) but, however, in the former, benzoic acid was progressively detected through time, reaching up to 40 mg/L after 24 h of contact. These results confirm the reactivity between alcohol and gold and also show the participation of water on the gold selectivity since benzoic acid instead of benzaldehyde is the major by-product obtained (Hou et al., 2008). During the phenol experiment, by-products were never detected in the liquid media and TOC and phenol conversions were coincident. Thus, only adsorption, no reaction, was the contribution to the phenol disappearance. In conclusion, the different reactivity of phenols and alcohols with gold invokes the different gold activity in the CWAO.

Figure 5b shows the results obtained over both Au/C model catalyst and a bared activated carbon (Merck, ref.: 102514), in order to elucidate the activity manifested by gold. Both solids were previously saturated in the corresponding pollutant by mixing the pollutant solution with the catalyst in the same ratio as in the reaction in order to avoid the adsorption contribution to the disappearance of the pollutants. In general, Au/C (Au_{dp}=10.5 nm) exhibited lower activity than Au/Al_2O_3 (Au_{dp}=1.48±0.02 nm) catalyst, which shows that the WAO of organic compounds is a size-dependence reaction as concluded by Besson et al., (2003). The difference in the reactivity between the tested target pollutants and gold is again observed and even more acute now because Au/C does not provide activity with phenol (Figure 5b).

In order to study the durability of Au/Al_2O_3 catalysts, the spent sample after the oxidation of benzyl alcohol was re-used in a second cycle. The results are also depicted in Figure 5a. As can be observed, TOC and COD conversions were half reduced whereas benzyl alcohol conversion was still maintained after 4 h of reaction though a decrease from 71 to 47 h^{-1} is obtained in the initial TOF values. The analyses subjected to the fresh and spent catalysts reveal that gold content and particle size remain over use but carbonaceous material is deposited on the catalyst surface (the carbon weigth percentage reached 4% after two reaction cycles, as confimed by elemental analyses). The deposits are decomposed between 773 and 873 K (according to thermogravimetric analyses under air and inert atmosphere). Therefore, it is reasonable to assume the polymeric nature of the carbonaceous material, more considering the susceptibility of aromatic pollutants to polymerize at the CWAO conditions.

In view of the above discussion, the application of gold in CWAO must be carefully considered attending to the nature of the pollutant. Investigation must be addressed in order to enhance gold activity and increase durability, in particular when dealing with pollutants prone to polymerize. Based on the noble metal catalysts studies, the use of appropriate supports, such as ceria and mixtures of ceria with others oxides, could help in these duties. Also, carbon supports may be interesting when the gold particle size is small (< 5 nm). The use of gold bimetallic catalysts can be also an alternative. As shows in fine-chemistry reactions, gold activity can be enhanced by their collaboration with other noble metals (Hutchings, 2007; Sankar et al., 2009). The investigation about the nature of active sites and the reaction mechanism may provide criteria for optimizing the preparation of gold catalysts and the selection of the support. Obviously, the way towards the industrial application of gold requires experimental work on real wastewater.

Other Emerging Catalysts

More sophisticated catalysts are being developed looking particularly for supreme stability. Most of those novel catalysts are listed in Table 2. They are metals oxide nanostructures, perovskites and polyoxometalates.

A novel nanocasted Mn-Ce-oxide catalyst was tested in the CWAO of aniline in a trickle-bed reactor (Levi et al., 2008). In this case, opposite to the observations with metal oxides, acidification of the solution with HCl was necessary to avoid colloidization and leaching of the nanoparticulate catalyst components by complexation with aniline. This catalyst showed stable performance for over 200 h on stream.

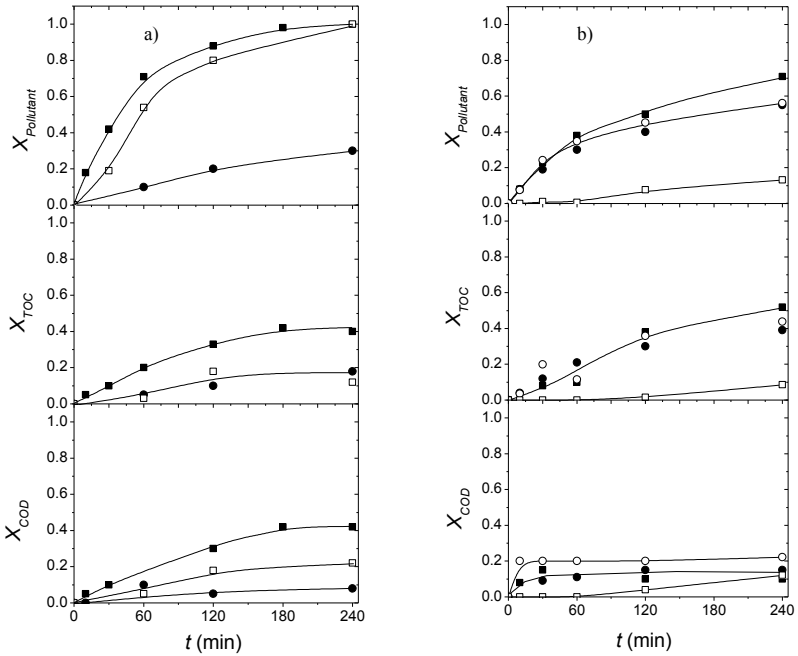

Figure 5. Activity of Au/Al_2O_3 (a) and Au/C and C (b) catalysts in the CWAO of benzyl alcohol (squares) and phenol (circles) expressed in terms of conversions. Reaction conditions: $C^{0}_{pollutant}$ =1 g/L, Q_{O2}=91.6 NmL/min, V_L=200 mL, *pH*=10, w_{cat}=0.5 g, *T*=398 K, p_{O2}=6 atm. Key: (a) ■ fresh catalyst; □ re-used catalyst; (b) closed symbols for Au/C and opened symbols for C. Lines to guide the eye.

The perovskite-type catalysts $LaFeO_3$, $LaCoO_3$ and $LaMnO_3$ prepared by the sol-gel method, have been also presented as novel catalysts (Yang et al., 2007; Royer et al., 2008). Their stability must be studied in each particular case. For instance, Yang et al., (2007) reported activity and structure stability of $LaFeO_3$ in the CWAO of salicylic acid and sulfonic salicylic acid only at T<413 K and Royer et al. (2008) observed the collapse of the $LaCoO_3$ and $LaMnO_3$ structures in the oxidation of stearic acid because of the formation of stable bulk carbonates with lanthanum.

Polyoxometalates, also named heteropolyacids, are oxo-clusters of early transition metals (groups 5 and 6) in their highest oxidation states, namely molybdenum, wolfram or vanadium. They represent an increasingly important class of environmentally benign catalysts that can be used at room temperature for the abatement of water pollutants at low concentrations (COD<200 mg/L). For instance, $Zn_{1.5}PMo_{12}O_{40}$ nanotubes have been synthesized for the wet oxidation of Safranin-T, a hazardous textile dye (Zhang et al., 2009), and micellar catalysts $[(C_nH_{2n+1})N(CH_3)_3]^{3+}{}_xPV_xMo_{12-x}O_{40}$ (x=1, 2, 3; n = 8–18) for phenol (Zhao et al., 2010).

CONCLUSIONS

Catalytic wet air oxidation is a developed technology with demonstrated industrial applications. The search for active and stable solid catalysts capable of working at milder operation conditions is an ongoing challenge. In this scenario, wet air oxidation opens new opportunities for the commercial exploitation of nanomaterials such as carbon nanostructures and gold nanoparticles as catalysts. The better knowledge about the chemistry of carbon along with the existing large-scale manufacturing of carbon nanostructures have led to a faster proliferation of research on these materials than on gold. Xerogels are presented as powerful catalysts. Good activity and adequate stability are reported in the few papers existing so far but long-term experiments in continuous mode are claimed for a better knowledge on their stability. Research on the potential application of gold in CWAO is still incipient but deactivation is identified as an important limitation, which opens the door to the use of gold bimetallic catalysts, as occurs for some fine-chemistry reactions. Cost-effective manufacturing and outstanding catalytic performance must be still demonstrated by the nanocatalysts to allow their widespread application in wet oxidation.

ACKNOWLEDGMENTS

The authors acknowledge the Ministerio de Ciencia e Innovación (MICINN) of Spain for the financial support through the projects CTQ2008-03988 and CTQ-2010-14807.

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Apéndice IV

Contribuciones a congresos

Presentaciones Orales:

2013 Carbon blacks as efficient and stable catalysts for catalytic wet peroxide oxidation. **C. M. Domínguez**, P. Ocón, A. Quintanilla, J. A. Casas, J. J. Rodriguez. 3rd European Conference on Environmental Applications of Advanced Oxidation Process-EAAOP-3 (Almería, Octubre 2013).

2013 Uso de la Voltametría Cíclica para evaluar la actividad catalítica de materiales carbonosos en la reacción de descomposición de peróxido de hidrógeno. **C. M. Domínguez**, A. Quintanilla, P. Ocón, J. A. Casas y, J. J. Rodriguez. Reunión del Grupo Español del Carbón, GEC (Madrid, Octubre 2013).

2011 Carbones Activados como Soportes de Nanopartículas de Oro en Procesos de Oxidación Húmeda con H_2O_2. A. Quintanilla, S. García-Rodríguez, **C. M. Domínguez**, S. Blasco, J. A. Casas, J. J. Rodriguez. Reunión del Grupo Español del Carbón (Badajoz, Noviembre 2011)

2011 Empleo de Negros de Humo como Catalizadores en Procesos de Oxidación Húmeda con Peróxido de Hidrógeno. **C. M. Domínguez**, A.

Quintanilla, N. Alonso-Morales, M. A. Gilarranz, J. A. Casas, J. J. Rodriguez. Reunión de la Sociedad Española de Catálisis, SECAT (Zaragoza, Junio 2011)

2010 Empleo de Catalizadores de Carbón en Procesos de Oxidación Húmeda con Peróxido de Hidrógeno. A. Quintanilla, A. Rey, **C. M. Domínguez**, N. Alonso-Morales, M. A. Gilarranz, J. A. Casas, J. J. Rodriguez. Congreso Nacional de Ingeniería Química-CNIQ, (Madrid, Noviembre 2010)

2009 Catalytic Wet Peroxide Oxidation of Organic Pollutants by Gold. A. Quintanilla, **C. M. Domínguez**, S. Blasco, J. A. Casas and J. J. Rodríguez. 2nd European conference on Environmental Applications of Advanced Oxidation Processes (Chipre, Septiembre 2009)

Presentaciones tipo póster:

2013 Gold nanoparticle catalysts for phenol wet peroxide oxidation. **C. M. Domínguez**, J. L. Díaz de Tuesta, S. García-Rodríguez, S. Blasco, A. Quintanilla, J. A. Casas, J. J. Rodriguez. 11th European Congress on Catalysis – EuropaCat-XI (Lyon, France, September 2013).

2012 Cyclic voltammetry as a tool for activity prediction of activated carbons for hydrogen peroxide decomposition in aqueous media. **C. M. Domínguez**, A. Quintanilla, P. Ocón, J. A. Casas, J. J. Rodriguez. International Congress of Chemical Engineering ANQUE-ICCE (Sevilla, Junio 2012)

2012 Winery wastewater treatment by hydrogen peroxide promoted wet air oxidation with carbon based catalysts. **C. M. Domínguez**, A. Quintanilla, P. Sanz, J. A. Casas, J. J. Rodriguez. AOP6 - 6th IWA-Conference on Oxidation Technologies for Water and Wastewater Treatment (Goslar, Mayo 2012)

2011 Activated carbons as efficient wet peroxide oxidation catalysts for phenol removal. **C. M. Domínguez**, A. Quintanilla, J. A. Casas, J. J. Rodriguez. 12th Mediterranean Congress of Chemical Engineering (Barcelona, Octubre 2011)

2011 Carbon Black catalysts for wet peroxidation processes. **C. M. Dominguez**, A. Quintanilla, N. Alonso-Morales, M. A. Gilarranz, J. A. Casas, J. J. Rodriguez. 4th International Conference on Carbons for Energy Storage/Conversion and Enviroment Protection (Vichy, Septiembre 2011)

2010 Catalytic Wet Peroxide Oxidation of high-loaded phenolic wastewaters by gold catalysts. A. Quintanilla, S. García-Rodríguez, **C. M. Domínguez**, S. Blasco, J. A. Casas, J. J. Rodriguez. 19th International Congress of Chemical and Process Engineering CHISA 2010 and 7th European Congress of Chemical Engineering – ECCE-7 (Praga, Agosto 2010).

Apéndice V

Otras contribuciones a congresos

Presentaciones Orales:

2009 Nuevos MOFs de cationes de tierras raras y de cationes alcalinotérreos. A. Monge, N. Snejko, F. Gándara, A. Platero-Prats, **C. M. Domínguez**, S. Gómez, E. Gutiérrez-Puebla, XII Encuentro de Química Inorgánica (Antofagasta, Chile, Enero 2009), Conferencia invitada.

2008 Híbridos órgano-inorgánicos para diodos LED. **C. M. Domínguez**, S. Gómez, A. Monge, E. Gutiérrez-Puebla. I Reunión de la Factoría de la Cristalización (Girona, Abril 2008).

Presentaciones tipo póster:

2013 Imidazolium-based ionic liquids breakdown by Fenton oxidation: ecotoxicity study. **C. M. Domínguez**, M. Munoz, A. Quintanilla, Z. M. de Pedro, S. P. M. Ventura, J. A. P. Coutinho, J. A. Casas, J. J. Rodriguez. 3rd European Conference on Environmental Applications of Advanced Oxidation Process-EAAOP-3 (Almería, Octubre 2013).

2013 Degradation of Ionic Liquids by Fenton Oxidation. M. Munoz, **C. M. Domínguez**, Z. M. de Pedro, A. Quintanilla, J. A. Casas, J. J. Rodriguez. 3rd European Conference on Environmental Applications of Advanced Oxidation Process-EAAOP-3 (Almería, Octubre 2013).

2013 Materiales carbonosos como catalizadores en procesos de oxidación húmeda con peróxido de hidrógeno para la eliminación de líquidos iónicos. M. Munoz, **C. M. Domínguez**, G. Pliego, Z. M. de Pedro, A. Quintanilla, J. A. Casas y J. J. Rodriguez. Reunión del Grupo Español del Carbón, GEC (Madrid, Octubre 2013).

2013 Preparation of $Cu/ZnO/Al_2O_3$ coatings in capillary reactors. J. L. Díaz de Tuesta, **C. M. Domínguez**, A. Quintanilla, J. A. Casas, J. J. Rodriguez. 11th European Congress on Catalysis – EuropaCat-XI (Lyon, France, September 2013).

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2012 Supported Gold Nanoparticles for Catalytic Wet Air Oxidation. A. Quintanilla, **C. M. Domínguez**, J. A. Casas, J. J. Rodriguez. 15th International Congress on Catalysis 2012 (Munich, Julio 2012).

2011 Wet oxidation processes for the treatment of sulfonation plant wastewater: evaluation of alternatives. J.L. Díaz de Tuesta, **C. M. Domínguez**, M. Montilla, A. Quintanilla, J.A. Casas, J.J. Rodriguez. 12th Mediterranean Congress of Chemical Engineering (Barcelona, Octubre 2011)

2011 El Oro en Procesos de Oxidación Húmeda Catalítica. A. Quintanilla, G. de Frutos, **C. M. Domínguez**, J. A. Casas, J.J. Rodriguez. Reunión de la Sociedad Española de Catálisis, SECAT (Zaragoza, Junio 2011).

2008 3D-Mesoestructured Sulfonic Acid Functionalized Silicas: Catalytic Implications. G. Morales, J. A. Melero, R. van Grieken, **C. M. Domínguez**. 6th International Mesostructured Materials Symposium (Namur, Septiembre 2008).